DESIGN OF ADVANCED W-BASED AND FE-BASED ALLOYS VIA
COMPUTATIONAL STUDY OF CRYSTALLINE DEFECTS

A Dissertation in
Materials Science and Engineering

by

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2016
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ABSTRACT

The mechanical properties and strength mechanisms in structural alloys are strongly dependent on crystalline defects (e.g., vacancies, solute atoms, dislocations, grain boundaries and interfaces), as well as the precipitates inherent in the microstructure. This thesis investigated some of the crystalline defects and precipitate phases in the W-based and Fe-based alloys via first-principles approaches in order to advance and advocate the design of these alloys for structural applications at elevated temperatures.

The poor formability of BCC (body-centered cubic) W at low temperatures is one of the major obstacles limiting its range of applications, such as the structural components for nuclear fusion reactors. The primary alloying element for increasing the ductility of W is recognized to be Re which is scarce and extremely expensive. Therefore, in order to identify alternative alloying elements for the development of W-based alloys with similar or improved mechanical properties, it is desirable to gain a fundamental and systematic understanding of alloying effects on the elasticity and plasticity of W as a function of temperature and alloying content. In this dissertation, the influence of various transition alloying elements on the elastic properties of W-based alloys via first-principles calculations is investigated first. Nineteen transition metal alloying elements are considered: Ti, V, Cr, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. It is found that (i) the bulk modulus of the dilute W-X alloy decreases with increasing its equilibrium volume, particularly, for the alloying elements in the same period; (ii) the earlier and later transition elements (e.g., Y, Zr and Pd) have stronger effects on the shear moduli than the other elements (e.g., Cr and Mo) which have the same number of valence
electrons as W; and (iii) the largest decrease of elastic properties of W is due to alloying with Y. In addition, it is shown that the changes of elastic properties of W caused by the alloying elements are traceable from the electron charge density distribution, resulting in a bonding distortion between W and the alloying atoms. Using the quasi-static approach based on the Debye model, the elastic properties of these W-X alloys at finite temperatures are predicted.

In addition to the alloying effects on the elasticity of W, the solute-induced softening and hardening effects in BCC W for twenty-one substitutional alloying elements (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt) are also examined to search for possible Re-substitutes that will result in a similar softening effect in W. The changes in the energy barriers and stress scales of dislocation motion caused by the solute-dislocation interactions are directly computed via first-principles approaches with special dislocation boundary conditions. The solute effects on critical resolved shear stress of the \( \frac{1}{2} <111> \) screw dislocation in BCC W at room temperature is quantitatively predicted, as a function of alloy concentration, via an improved mesoscopic solid-solution model by using first-principles results as input parameters. It is found that the solute elements, which induce large reductions in the shear modulus or bulk/shear moduli ratio, do not necessarily decrease the plastic/flow strength of BCC W. Al and Mn are proposed to be promising substitutes for Re as these two elements introduce a similar softening effect as Re in BCC W. In addition, the trends, regularities of the solute-dislocation interactions, and their correlations to the dislocation core structure geometries are discussed.
Ferritic alloys are among the most important structural engineering alloys in our society. Application of ferritic alloys in extremely harsh environments as structural components, such as high-pressure steam piping and nuclear reactors, require strength capabilities at elevated temperatures. By drastically reducing the grain size (< 100nm), grain boundary (GB) strengthening can be an efficient way to enhance the hardness and strength of ferritic alloys. However, the additional energy associated with large amount of GB area induces a strong driving force for grain growth, resulting in loss of GB strengthening at high temperatures. Segregation of specific solute elements at GBs is perceived to be one of the most effective ways to mitigate grain growth at high temperatures in nanocrystalline ferritic alloys. It is believed that the GB energy could be remarkably reduced via solute segregation and thus the capillary driving force for grain growth. In this part of the dissertation, first-principles calculations based on density functional theory (DFT) are performed to understand the atomistic mechanisms of the solute-GB interactions. The segregation effects of six transition metal elements (Cr, Ni, Cu, Zr, Ta and W) on the Σ3 (111)[110] tilt boundary in BCC Fe are systematically investigated by examining the GB energy, GB area, solute segregation energy and GB cohesion. It is found that the GB energy reduction is more related to the solute segregation energy than the GB area extension. The solute segregation energy is verified to be composed as a combination of the strain and chemical contributions, even for the solute elements with large atomic volumes. The dynamic changes in atomic and electronic structures in response to the applied strains are investigated to provide physical insight into the effects of solute segregation on the GB cohesion.
Alternatively, creating and maintaining precipitates coherent with the host matrix, under service conditions is one of the most effective approaches for successful development of alloys for high temperature applications. In this part of the dissertation, a new, nano-sized superlattice (NSS) phase in ball-milled Fe alloys, which maintains coherency with the BCC matrix up to at least 913°C, has been discovered. As a result, a new, nano-scale coherent precipitate strengthening phenomenon is observed in this class of ferritic alloys. First-principles calculations using various exchange-correlation functionals are performed to investigate the crystal structure and stabilization mechanisms of these clusters. It is proposed that this phase is metastable and has a chemistry of Fe₃O and a D₀₃ crystal structure. In addition to elucidating the crystal structure, the role of Zr in stabilizing this as-observed precipitate phase is understood by the analysis of chemical bonding between Zr and O atoms.

Overall, the present thesis provides an in-depth study of the effects of alloying elements on the mechanical and thermodynamic properties of W-based alloys and Fe-based alloys. The results and conclusions would enable the future development of these two alloys systems for applications at elevated temperatures.
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ACKNOWLEDGEMENTS

This dissertation could not have been accomplished without help and support. There are many people I gratefully acknowledge.

I would like to express my sincere thanks to my PhD advisor Dr. Zi-Kui Liu, you have been a tremendous mentor for me. I want to thank him for the continuous support of my Ph.D. study and his patience, motivation, and immense knowledge. Dr. Liu has inspired me with his enthusiasm to materials science, his ways of solving problems and his attitude to life. I sincerely appreciate all he has done for me.

Besides my advisor, I would like to thank rest of committee members, Dr. Allison M. Beese, Dr. Hojong Kim, Dr. Vincent H. Crespi, Dr. Laszlo J. Kecskes and Dr. Kristopher A. Darling for their time, encouragements and suggestions during serving on my dissertation committee.

Many thanks to Dr. Laszlo J. Kecskes, Dr. Kristopher A. Darling and Mr. Brady G. Butler for their valuable comments and suggestions on my research work, and generous help on my manuscript writing.

I would like to thank all my colleagues in the Phases Research Lab, especially Dr. Shunli Shang, Dr. Yi Wang, and Dr. William Yi Wang for helping me get footed. Additional thank goes to Dr. Bi-cheng Zhou, Dr. Xuan Liu and Austin Ross for their valuable discussions and teaching me using ThermoCalc. Many thanks to Dr. Weiwei Xu for the discussions on first-principles tensile simulations. I also want to thank the help and encouragement from Richard Otis, Cassie Maker, Pinwen Guan and Hongyeun Kim.
I would like to thank all my friends in State College, especially Kai Shen, Bi-Cheng Zhou and Chen Chen. Because of you guys, my Ph.D life here was colorful and enjoyable. All the great time we shared will be my cherished memories.

Lastly, I would like to express my deepest thanks to my parents, Dr. Zhongai Hu and Hongying Wu, and my significant other, Yuanting Chen. Your unconditional love and understanding is always my unlimited source of inspiration and power when I am facing challenges. I could not have done this without them. I owe most of my accomplishments to them.
Chapter 1

Introduction

1.1 Motivation

The ever-increasing demand for higher energy efficiency continuously pushes the properties of structural alloys towards greater strength, higher toughness, and better resistance to high temperature environments. In this context, to expedite the development and design of new structural alloys with high performance is both timely and important. The large design spaces in compositions, temperatures and pressures make traditional trial and error metallurgy become prohibitively expensive and time consuming. Meanwhile, the strengthening and deformation mechanisms behind, which are strongly related to the crystalline defects in the alloys (e.g., vacancies, solutes, dislocations, grain boundaries and interfaces), require further understanding. Owing to advances in computational science, advanced alloy design and development are shifting toward a new paradigm based on integrated computational-prediction and experimental-validation approaches. Furthermore, effects of crystalline defects and precipitate phases on the mechanical properties of the matrix phase can now be studied via computational techniques in a new light, such as at the atomic scale, to develop better understanding of alloy strengthening
and deformation mechanisms. The aim of the present dissertation is to generate new knowledge and better understanding of some of these effects in W-based and Fe-based alloys via first-principles approaches.

BCC W and its alloys are a class of materials with high melting temperature, high density, strong mechanical properties and good resistance to gamma and neutron radiation. However, further applications of these alloys, such as the structural components for fusion power plants, have been mainly limited by the brittle deformation behavior at low temperatures resulting from poly-crystalline W’s high ductile-to-brittle transition temperature (DBTT); for example, the DBTT of wrought and recrystallized W sheets varies between 280 °C to 370 °C [1]. The poor formability of W-based alloys at low temperatures makes the processing difficult and costly. Decreasing the DBTT, and correspondingly enhancing the low temperature ductility of W, is considered to be the most direct route in improving the formability of W. In addition, it will also open a gate for W-based alloys to be used as structural materials at ambient environments.

Currently, in order to further increase the ductility and formability, the primary alloying element for BCC W has been Re [1–3]. However, Re is one of the least abundant elements in the Earth’s crust, resulting in its extremely high price [4]. In response to this dilemma, there is significant on-going research to identify alternative alloying elements for the development of W-based alloys with similar or improved mechanical properties. Therefore, it is desirable to gain a fundamental understanding of systematic alloying effects on mechanical properties of W as a function of temperature and alloy content. Elasticity could be a good starting point as it describes the early stage of deformation which reflects the material’s capability to recover its original shape after mechanical loading.
Understanding the effects of alloying elements on elasticity may help us to gauge their effects on plasticity as well. For instance, the reduction in the elastic shear moduli can be interpreted as a form of lattice softening induced by the alloying elements, as reflected by ideal shear strength changes [5–7]. In addition, the elasticity of single crystals and the associated polycrystalline aggregate properties can provide information about a vast number of material-related behaviors, such as mechanical anisotropy and stability [5], Debye temperature [6], hardness [7], melting temperatures [8], ductility/brittleness [9], and creep rate [10]. Therefore, a systematic study of the alloying effects on the elastic properties of BCC W is necessary and important.

It is found that the improvement on ductility in W induced by Re is always accompanied with reductions in yield strength. This phenomenon is well known as the solid-solution softening (SSS) phenomenon, which results from the interactions between the solute atoms and dislocations [8]. This solute induced SSS phenomenon has been experimentally well-studied back in the 70s, not only in W, but also in other BCC metals, in which the dislocation mobility is controlled by the kink nucleation and migration since the Peierls relief is quite high [3,9–13]. In addition to Re, some other 5d precious metal elements (i.e., Os, Ir and Pt) have been found to have the softening effects as well but with different alloying concentrations [3,9,14,15]. It is believed that the dislocation mobility is promoted by lowering the energy barrier of double-kink nucleation at the solute sites, consequently leading to a decrease of plastic strength [8,16]. Mesoscopic models have been developed previously based on the continuum elasticity theory to describe the solute-dislocation interactions in terms of the differences of atomic radii or elastic moduli between the solute and solvent atoms [8,16,17]. However, the experimental results for the BCC
refractory metals indicate that the size/elastic mismatch cannot be considered as the main parameters responsible for the SSS phenomenon. For instance, it is found that Re, Os, Ir and Pt solutes lead to yield strength softening in BCC Mo and the softening potency does not correlate with atomic radii [3,9,18]. In fact, the SSS behavior is believed to be mainly attributed to the effects of solutes on the electronic structure of the dislocation when the solute is exactly inside the dislocation core where the continuum elasticity theory is incorrect [19,20]. Therefore, capturing the electronic interactions between the solutes and dislocation at atomic scale accurately could be the key to understand the mechanism of the solute induced SSS in BCC W. Moreover, the alternative elements to Re may be found by having the similar softening effects as Re in BCC W.

For ferritic alloys, further improving and maintaining the strength under service conditions are quite important. Nanocrystalline BCC Fe possess extremely high strengths due to the contribution of GB strengthening (i.e., the Hall-Patch effect) [21–23]. However, a fundamental limitation to their applications arises from their poor heat resistance by losing the feature of small grain size. The excess energy associated with the large amount of GB area results in an enormous driving force for grain growth at elevated temperatures. For example, two orders of magnitude increase of the grain size has been observed for the nanocrystalline Fe after one hour annealing treatment at 700 °C [22,24]. Consequently, the mechanical enhancement from the GB strengthening is lost. This grain growth phenomenon can be a significant obstacle for high temperature applications. Small additions of some insoluble elements (i.e., solute) has been experimentally explored to stabilize the grain size of BCC Fe at a nanoscale to effectively withstand high temperature environment [22,24]. The solute is initially forced into the solution phase by
nonequilibrium processing (e.g., mechanical alloying, rapid solidification, etc.), and then, upon heating, segregates to GBs or precipitates out as a second phase. There are two basic mechanisms known for the solute stabilization effects in terms of kinetic and thermodynamic. For the kinetic stabilization mechanism, the GB mobility by diffusion-related processes is hindered by solute drag or via pinning effects of precipitates [25,26]. For the thermodynamic stabilization, it is believed that the segregation of solutes results in reductions in GB energy and thus the driving force for grain growth [27–37]. Since the mobility is thermally activated, the drag or pinning effects become weak when temperature increases [38]. On the other hand, the thermodynamic approach of stabilization can be more effective at high temperatures since the GB energy is expected to have a weaker temperature dependence [22,37].

In order to predict the energetics of solute segregation and thermal stability in nanocrystalline alloy systems, various analytically thermodynamic models have been developed [27,28,31,35–37,39,40]. In these models, the solute segregation enthalpy, which is one of the key parameters to determine the GB energy, is usually estimated empirically [35]. The estimation generally involves two contributions: one is the strain contribution due to the strain releasing caused by solute segregation, based on the misfit of atomic size and elastic modulus [35,41–43]; another is the chemical contribution attributed to the difference between the atomic bonds at the GB and in the grain interior [35,41,42,44]. The solute segregation enthalpy is considered to be the strain contribution [43], or the chemical contribution completely [44], or a combination of these two contributions [41,42]. In addition, the individual atomic interactions between the solute and solvent are treated to be the same at the GB and in the grain interior in some models [31,37,45], where the chemical
contribution mainly depends on the disparities between the atomic coordination numbers in and out of the GB plane [42]. Furthermore, there are approaches that distinguish the solute-solvent interactions at GB from that of grain interior to estimate the chemical contribution more rigorously, but with an increased calculation complexity [40]. All these models have been applied to ferritic systems and a wide range of other binary alloy systems with varying degrees of success. However, the discrepancies between the descriptions of the segregation enthalpy necessitate an investigation of the interaction between the solute elements and GBs in more details.

On the other hand, creating and maintaining precipitates coherent with the host matrix, under service conditions is another effective strengthening mechanisms in alloys. The precipitates can be either thermodynamically stable or meta-stable. The full coherency between the precipitates and matrix leads to strengthening by mechanisms such as the creation of antiphase boundaries or coherency strains that impede dislocation motion [8,46]. More importantly, coherency gives rise to low interfacial energies between the precipitates and matrix, thus increasing thermal stability by significantly reducing coarsening [47] or the transitioning to incoherency, i.e., over aging [48]. As a result, these strengthened alloys are known to preserve their excellent mechanical properties at elevated temperatures.

The successful cases include age-hardened Al-based alloys and Ni-based superalloys. For Al-based alloys, the coherent precipitates include the metastable Guinier-Preston zones and a series of metastable phases, while for Ni-based superalloys, it is the stable L12 precipitates, both within the FCC matrix [46,49–51]. In ferritic alloys, no reliable coherent precipitates stable at high temperatures have been found. BCC-Cu precipitates in
the Fe-Cu system and β’ (NiAl-type) precipitates in the Fe-Ni-Al system have been explored via aging due to their lattice coherency with the BCC Fe matrix. Unfortunately, it was found that BCC-Cu easily transforms to FCC at 550 °C, inducing harmful brittleness [52]. Likewise, the rapid decrease of yield strength around 600 °C and high coarsening rates impede the application of NiAl-strengthened ferritic alloys at high temperatures [53,54]. In contrast to conventional aging methods, mechanical alloying provides alternative possibilities in the search and creation of precipitates, because of its capability to synthesize highly supersaturated solid solutions and metastable intermetallics [55,56]. Recently, our collaborators performed experiments with ball-milled Fe and Fe-Zr alloys, and found a new, oxygen-enriched, nano-cluster precipitate phase in these alloys. These precipitates maintain lattice coherency with the BCC Fe matrix up to at least 913 °C, and can be further stabilized by the addition of Zr. In addition to the GB strengthening, substantial strength improvements have been observed in these alloys, which are considered to be the strengthening effects from these nano-precipitates. However, the crystal structure and thermodynamic stability of this precipitate phase and the role of Zr in this phase still need to be further investigated and understood.

The state-of-the-art quantum-mechanical method based on density functional theory [57–60], so-called first-principles approach, provides a perfect platform to address the issues discussed above. This method directly computes the electronic interactions with arbitrary atoms at the atomic scale in a periodic supercell by only inputting the atomic types and coordination, and does not rely on any experimentally fitted or empirical parameters. By building the crystalline defects in the input crystal structure, we would be able to calculate the electronic structures of these defects and study their effects on the matrix
phases. To predict elastic properties of W-based alloys, an efficient stress-stress method developed by Shang et al. [61] will be utilized based on the outputs from first-principles calculations. One limitation of the DFT-based first-principles calculations is that it cannot adapt systems with large number of atoms (over 500 atoms) efficiently since the calculation computationally is very time consuming. This restricts the modeling of the crystalline defects which requires a self-consistent coupling of the defect center to the long-range elastic field. Therefore, to compute the properties of dislocations, a special dislocation boundary method developed by Trinkle and Woodward et al. [62,63] will be incorporated, which can well treat the long-range elastic field generated by the dislocation in a reasonable supercell size. To accurately calculate the phase stability and energy quantities, such as the solute segregation energy, grain boundary energy and cohesive energy, appropriate models have to be utilized to obtain reliable energy differences, such as the equation of state (EOS) fittings [61,64]. For the physical properties at finite temperature, the quasi-harmonic approximation based on the Debye model [65–67] will be utilized. The details of the methods and models used in this dissertation will be presented in Chapter 2.

1.2 Overview

The overarching goals of the present dissertation are to investigate the effects of alloying elements on the elastic and plastic properties of W-based alloys, as well as the solute segregations on GB and precipitate phases in Fe-based alloys via DFT based first-principle calculations. The rest of the dissertation is organized as follows:
In Chapter 2, the computational methods and theories in the present dissertation are discussed in detail, including the background and details for all type of first-principles calculations, and the flexible boundary condition method for modeling dislocations. Last, but not least, the method for viewing the dislocation core geometry is introduced.

In Chapter 3, the effects of alloying elements on the elastic properties of BCC W are investigated systematically as a function of temperature, including isothermal and isentropic elastic stiffness components, bulk modulus, shear moduli, Young’s modulus, and elastic anisotropy. Nineteen transition metal alloying elements are considered: Ti, V, Cr, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. In addition, the trends, regularities of the predicted elastic properties, and their electronic origins are discussed.

In Chapter 4, the solute-induced softening and hardening in BCC W is studied for twenty-one substitutional alloying elements, namely Al, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt, to search possible substitutes for Re that will result in a similar softening effect in W. The changes in the energy barriers and stress scales of dislocation motion caused by the solute-dislocation interactions are directly computed via first-principles approaches with special dislocation boundary conditions. The solute effects on the critical resolved shear stress of the $\frac{1}{2} <111>$ screw dislocation in BCC W at room temperature is quantitatively predicted, as a function of alloy concentration, via an improved mesoscopic solid-solution model by using first-principles results as input parameters. In addition, the trends, regularities of the solute-dislocation interactions, and their correlations to the core structure geometries are discussed.

In Chapter 5, the segregation effects of six transition metal elements (Cr, Ni, Cu, Zr, Ta and W) on the $\Sigma 3 (111)[1\bar{1}0]$ tilt boundary in BCC Fe are investigated
systematically via first-principles calculations in terms of the GB energy, GB area, solute segregation energy, and GB cohesion. The quantification of the solute segregation energy is discussed in terms of the crystalline lattice distortion and the chemical bond energies between in and out of the GB region. The dynamic changes in atomic and electronic structures in response to applied tensile strains are investigated to provide physical insight into the effects of solute segregation on the failure mechanisms of the $\Sigma3 (111)[1\overline{1}0]$ tilt boundary in BCC Fe.

In Chapter 6, we first present the experimental evidences for the Fe-O nano-precipitates in ball-milled Fe and Fe-Zr alloys. Then, the crystal structure and thermodynamic stability of the precipitate phase are discussed, based on the results of first-principles calculations. Last, the role of Zr in stabilizing the precipitate phase is investigated in the view of electronic structures.

Finally, Chapter 7 concludes this thesis by presenting a summary of all of the work done and provides some thoughts on future work.
Chapter 2

Methodology

2.1 First-principles calculations based on density functional theory

The primary computational method used in this dissertation is density functional theory (DFT) based first-principles approach, which is also known as “ab-initio calculations.” This method computes the interactions with arbitrary atoms at atomic scale in a periodic supercell using quantum mechanical electronic theory based on the electronic charge density. Meaning from “first principles or ab-initio” is because the inputs for the calculations do not require to any empirical potential or experimental data, but only atomic coordination and types. Therefore, via building the input crystalline structures with various defects, such as solute atoms, grain boundaries and dislocations, we would be able to compute the fundamental properties of these defects and their effects in the bulk matrix.

In the following sections, we will first give a basic introduction of the density functional theory. Then, some special techniques based on the DFT first-principles calculations are described in the later sections.
2.1.1 Density functional theory

The interactions of the positively charged nuclei and negatively charged electrons in a crystalline structure are considered to be a many-body problem. In principle, a quantum mechanical solution to this problem can be obtained by solving the Schrödinger’s equation involving both nuclei and electrons. The time-independent, non-relativistic Schrödinger equation for an N-electrons system can be written as,

**Equation 2.1** \[ \hat{H}\Psi = E\Psi \]

where \( E \) denotes the system energy, \( \Psi \) denotes the many-body wave function of electrons in the system and \( \hat{H} \) denotes the Hamiltonian operator given by,

**Equation 2.2** \[ \hat{H} = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - e^2 \sum_a Z_a \frac{1}{|\vec{r}_i - \vec{R}_a|} + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right) \]

where \( N \) is the total number of electrons in the system, \( m \) is the mass of a single electron. \( \vec{r}_i \) denotes the position of electron \( i \) and \( \vec{R}_a \) denotes the position of nuclear \( a \) with a charge valance of \( Z_a \). In this expression, the first term is many-body kinetic energy operator. Based on the Born-Oppenheimer approximation, the motion of nuclei and electrons can be considered separately. Since the mass of atomic nuclei is much larger than that of electrons (~ \( 10^3 \) to \( 10^5 \) times larger), the motion of atomic nuclei in the electronic timescale can be ignored. Therefore, in Equation 2.2, all the nuclei is assumed to be stationary and clamped at their positions. The second term represents the Coulomb interactions between the atomic nuclei and electrons, while the third term accounts for the electron-electron interactions.
Equation 2.2 is solved for wave function $\Psi$ subject to antisymmetric constraints with the energy eigenvalues in which the lowest one is the ground state energy. However, directly solving Equation 2.2 is usually intractable, except in the trivially simple case, for mainly two reasons: first, the many-body system results in too many variables in the wave-function (3N degrees of freedom); second, the electron-electron Coulomb interaction make the electronic motions being correlated.

DFT provides a way to systematically map the many-body electron problem on to a single-body problem based on the density of electron, which is a function of only three variables, i.e., the three Cartesian directions. Here we employed the Hohenberg-Kohn-Sham formulation of DFT [68,69], which is based on the so-called Hohenberg-Kohn theorems [68],

Theorem I: the external potential is a unique functional of the electron density only, which means the Hamiltonian in Equation 2.2 is solely determined by the electron density.

Theorem II: the ground state energy of the system may be obtained variationally: the density that minimizes the total energy is the exact ground state density.

Since the Hamiltonian fixes the ground state of the system under consideration, the solution of many-body wave-function in Schrödinger equation for ground state is also unique to the ground state electron density. Therefore, the total energy functional of a many-body electron system can be written as a function of electron density $\rho(\vec{r})$,

**Equation 2.3**  
$$ E[\rho(\vec{r})] = T[\rho(\vec{r})] + \int V_{\text{ext}}(\rho(\vec{r}))\rho(\vec{r})d^3r + E_{ee}[\rho(\vec{r})] $$

where $T$ is the kinetic energy and $E_{ee}$ is the electron-electron interaction energy, while the $V_{\text{ext}}$ denotes the external potential of the system, mainly the nuclei charge field. In order to
solve the electron density $\rho(\vec{r})$, Kohn and Sham introduce a fictitious system (known as the Kohn-Sham system) of non-interacting electrons that generate the same density as the real system with electron interactions [69]. In the Kohn-Sham system, the $\rho(\vec{r})$ of $N$ electrons is expressed as [69],

**Equation 2.4**  \[ \rho(\vec{r}) = \sum_{i}^{N} |\phi_{i}(\vec{r})|^2 \]

where $\phi_{i}(\vec{r})$ is the Kohn-Sham orbital which is the solution of the Kohn-Sham equation,

**Equation 2.5**  \[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(\vec{r}) + V_{Hartree}(\vec{r}) + V_{xc}(\vec{r}) \right] \phi(\vec{r}) = \epsilon_{i} \phi(\vec{r}) \]

where the $\epsilon_{i}$ is the orbital energy of the corresponding Kohn-Sham orbital. In the equation, $V_{ext}(\vec{r})$ is the potential accounting for the electron-nuclei interaction which has the same form as Equation 2.2. $V_{Hartree}(\vec{r})$ defines the Coulomb electron-electron interaction, including the self-interaction, which is a unique functional of the electron density,

**Equation 2.6**  \[ V_{Hartree}(\vec{r}) = e^2 \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} d^3\vec{r} \]

The last term $V_{xc}(\vec{r})$ is the exchange-correlation potential, which accounts for the unphysical self-interaction error, alongside with other effects. This term is the only unknown in the Kohn-Sham equation which is the derivative to its energy expression with respect to $\rho(\vec{r})$,

**Equation 2.7**  \[ V_{xc}(\vec{r}) = \frac{\partial E_{xc}(\rho(\vec{r}))}{\partial \rho(\vec{r})} \]
Unfortunately, the exchange-correlation energy has no explicit analytical form so that approximate functionals based upon the electron density must be introduced to describe this term. The approximation solely depends on the value of $\rho(\vec{r})$ at a coordinate in space is known as the local density approximation (LDA) [59]. The exchange-correlation energy $E_{xc}(\rho(\vec{r}))$ is treated be same as the value of the uniform electron gas with same electron density [70]. Another widely used approximation is the generalized gradient approximation (GGA) which incorporates the effects of inhomogeneity by including the gradient of electron density [71]. In fact, efforts to develop efficient and accurate descriptions of the exchange-correlation term never stop, including modifying the implementations of GGA, orbital-dependent functional, and hybrid functional [72–74]. Various implementations of GGA have been developed, including PW91-GGA from Perdew and Wang [75], PBE-GGA from Perdew, Burke and Ernzerhof (PBE) [76], and revised PBE-GGA for solids (PBeSol) [77]. In general, the PW91-GGA and PBE-GGA give better predictions of the equilibrium properties for metallic systems. Based on these approximate exchange-correlation functionals, the Kohn-Sham equation can be solved based on iterative method. The DFT based first-principles calculations in the present work are performed using the well-established the Vienna ab-initio Simulation Package (VASP) [57].
2.1.2 Energy vs. volume equation of state (EOS)

The energy vs. volume equation of state (EOS) describes the dependence of the total energy of a crystalline structure on its volume. The EOS can be used to determine the equilibrium state of the input crystalline structure, and provide necessary parameters for the calculations of finite temperature properties [65–67]. In the present work, the EOS is obtained by fitting the first-principles total energy vs. corresponding volume based on a four-parameter Birch-Murnaghan EOS [61,66]:

\[
E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2}
\]

where \(a\), \(b\), \(c\) and \(d\) are fitting parameters from which the equilibrium energy \((E_0)\), volume \((V_0)\) bulk modulus \((B_0)\), and the first derivative of bulk modulus with respect to pressure \((B'_0)\) can be calculated.

As a rule of thumb, six to seven first-principles calculations at different volumes is necessary to obtain the EOS fitting. The volume range should be within ±5% around the equilibrium volume. A starting volume can be obtained from a volume-relaxation calculation for the input structure. For the elements with magnetism, care should be taken for the relationship between the magnetic moment and supercell volume; a sudden jump of the magnetic moment usually indicates a magnetic phase transformation or calculation setting abnormal.
2.1.3 First-principles elastic constants at 0K

Elastic stiffness constants in this dissertation are calculated based on the efficient stress-strain method [64] via first-principles calculations. Specifically, independent sets of strains are applied to deform the supercell in the elastic range. For a given set of strains, \( \varepsilon_i = \left( \varepsilon_{i,1}, \varepsilon_{i,2}, \ldots, \varepsilon_{i,6} \right) \), lattice vectors of the strained supercell, \( \mathbf{R}' \), in Cartesian coordinates can be calculated as,

\[
\mathbf{R}' = \mathbf{D}\mathbf{R} = \begin{pmatrix}
1 + \varepsilon_{i,1} & \varepsilon_{i,6}/2 & \varepsilon_{i,5}/2 \\
\varepsilon_{i,6}/2 & 1 + \varepsilon_{i,2} & \varepsilon_{i,4}/2 \\
\varepsilon_{i,5}/2 & \varepsilon_{i,4}/2 & 1 + \varepsilon_{i,3}
\end{pmatrix} \begin{pmatrix}
a_1 & a_2 & a_3 \\
b_1 & b_2 & b_3 \\
c_1 & c_2 & c_3
\end{pmatrix}
\]

where \( \mathbf{R} \) are the lattice vectors of the unstrained supercell. The stresses in response to the given strains are calculated via the aforementioned first-principles approach.

Generally, in order to calculate the complete elastic stiffness constants, six independent sets of strains are applied on the structure:

\[
\begin{pmatrix}
\varepsilon_{1,1} & \varepsilon_{1,6} \\
\varepsilon_{2,1} & \varepsilon_{2,6} \\
\varepsilon_{3,1} & \varepsilon_{3,6} \\
\varepsilon_{4,1} & \varepsilon_{4,6} \\
\varepsilon_{5,1} & \varepsilon_{5,6} \\
\varepsilon_{6,1} & \varepsilon_{6,6}
\end{pmatrix} = \begin{pmatrix}
x \\
x \\
x \\
x \\
x \\
x
\end{pmatrix}
\]

where \( x = \pm 0.01 \) in the present work, and the strain components not shown are zero. Using the six sets of corresponding stresses from first-principles, the elastic stiffness constants at a fixed volume, \( c_{ij}(V) \), can be determined based on Hooke’s law as follows:
For cubic crystals, there are only three independent elastic stiffness constants, \( c_{11} \), \( c_{12} \), and \( c_{44} \). Therefore, instead of six, only two linearly independent sets of strains are needed to calculate all the cubic elastic stiffness constants. In the present work, \( c_{11} \) and \( c_{12} \) are obtained from the set of strains, \( \varepsilon_1 \), and \( c_{44} \) is obtained from the set of strains, \( \varepsilon_4 \).

Based on the single crystal elastic stiffness constants obtained, aggregate properties of the bulk \( (B) \), shear \( (G) \), and Young’s \( (E) \) moduli and Poisson’s ratio \( (\nu) \) associated with polycrystals are estimated by means of the Voigt approximation [78]; this provides the upper bound of elastic properties in terms of uniform strains. For a cubic crystal,

**Equation 2.12** \[ B = \left( c_{11} + 2c_{12} \right) / 3 \]

**Equation 2.13** \[ G = \left( c_{11} - c_{12} + 3c_{44} \right) / 5 \]

**Equation 2.14** \[ E = 9BG / (3B + G) \]

**Equation 2.15** \[ \nu = (3B - 2G) / 2(3B + G) \]

The shear modulus along the closest-packed \(<111>\) direction is also calculated since this is the shearing direction for dislocation glide in BCC W [2]. For cubic crystals [5],

**Equation 2.16** \[ G_{111} = \frac{3c_{44} \left( c_{11} - c_{12} \right)}{c_{11} - c_{12} + 4c_{44}} \]
The universal elastic anisotropy index, $A^U$, can be calculated based on the Zener anisotropy ratio, $A^Z$. For a cubic crystal [79],

\[ A^U = \frac{6}{5} \left( \sqrt{A^Z} - \frac{1}{\sqrt{A^Z}} \right)^2 \]

where $A^Z = 2c_{44}/(c_{11} - c_{12})$[61]. $A^U = 0$ or $A^Z = 1$ indicates an isotropic crystal.

### 2.1.4 Thermodynamic and elastic constants at finite temperatures

The elastic stiffness constants at finite temperatures could be estimated by a quasi-static approach in terms of the predicted Helmholtz free energy at finite temperatures and the predicted elasticity as a function of volume at 0 K [80]. The Helmholtz free energy, $F(V,T)$, at volume $V$ and temperature $T$ can be calculated using the quasi-harmonic approach [66],

\[ F(V,T) = E(V) + F_{ele}(V,T) + F_{vib}(V,T) \]

The first part, $E(V)$, is a static energy at 0 K and, without the contribution of the zero-point vibration, it is obtained by a fitting of the first-principles energy vs. volume data points based on a four-parameter Birch-Murnaghan equation of state (EOS).

The second part in the Equation 2.18, $F_{ele}(V,T)$, represents the thermal electronic contribution [66,81]. This part is necessary due to the non-zero electronic density at the Fermi level associated with metals. The free energy contribution from the thermally activated electrons can be written as:

\[ F_{ele} = E_{ele} - TS_{ele} \]
where $E_{ele}$ and $S_{ele}$ are the energy and entropy of thermal electron excitations, respectively. The entropy term can be calculated via integrating the electronic density of states along with the distribution of the states over the energies of the electrons:

**Equation 2.20** \[ S_{ele}(V,T) = -k_B \int n(\varepsilon,V) \left[ \ln f(\varepsilon,T) + (1 - f(\varepsilon,T)) \ln (1 - f(\varepsilon,T)) \right] d\varepsilon \]

where $n(\varepsilon,V)$ is the electronic density of state at energy $\varepsilon$ and $f$ is the Fermi-Dirac distribution since electrons are fermions, and given by:

**Equation 2.21** \[ f(\varepsilon,T) = \left[ \exp \left( \frac{\varepsilon - \mu}{k_BT} \right) + 1 \right]^{-1} \]

where $\mu$ is the chemical potential of electrons. The energy term can be calculated by:

**Equation 2.22** \[ E_{ele}(V,T) = \int_{-\infty}^{\varepsilon_f} n(\varepsilon,V) f(\varepsilon,T) \varepsilon d\varepsilon - \int_{-\infty}^{\varepsilon_f} n(\varepsilon,V) \varepsilon d\varepsilon \]

where $\varepsilon_f$ is Fermi energy. In the present work, electronic DOSs are obtained from first-principles calculations.

The third part in Equation 2.18, $F_{vib}(V,T)$, is the contribution of lattice vibrations to the Helmholtz free energy. In the present work, for sake of simplicity and efficiency, the vibrational contribution is depicted based on the Debye-Grüneisen model [65,66],

**Equation 2.23** \[ F_{vib}(V,T) = \frac{9}{8} k_B \Theta_D + k_B T \left\{ 3 \ln \left[ 1 - \exp \left( -\frac{\Theta_D}{T} \right) \right] - D \left( \frac{\Theta_D}{T} \right) \right\} \]

where $k_B$ is the Boltzmann constant and $D(\Theta_D/T)$ the Debye function. The Debye temperature $\Theta_D$ can be calculated by,
Equation 2.24 \[ \Theta_p = s \left( \frac{6\pi^2}{5} \right)^{\frac{1}{3}} \frac{\hbar}{k_B} V_0 \left( B_0 / M \right)^{\frac{1}{3}} (V / V_0)^{\frac{1}{3}} \]

where \( M \) is the atomic mass and \( s \) a scaling factor which is calculated based on the Poisson’s ratio of pure \( W \) [65]. The Grüneisen constant, \( \gamma \), is defined as \( \gamma = \left[ (1 + B'_0) / 2 - x \right] \), with \( x = 2/3 \) due to the high melting temperature of \( W \) [66].

As temperature and volume are two independent variables of the Helmholtz free energy, the equilibrium volume at temperatures of interests, \( V(T) \), can be directly calculated from Equation 2.18. Combining this with the predicted elastic constants \( c_{ij}(V) \), the isothermal elastic stiffness constants at finite temperatures can be estimated as \( c_{ij}(T) = c_{ij}(V(T)) \) [79,80]. It should be mentioned that this approach assumes that the change of elastic stiffness mainly depends on the volume expansion and anharmonicity effects and contributions due to the fluctuation of microscopic stress tensors are not taken into consideration.

Generally, measured elastic constants obtained via the resonance method are isentropic because the elastic waves travel faster than the rate of heat conduction, leading to the measurements being adiabatic in nature. Therefore, in order to compare them with experiments, the calculated isothermal elastic stiffness constants need to be converted to the isentropic ones. For cubic crystals, the thermodynamic relationships between the isothermal \( c_{ij}^T \) and isentropic \( c_{ij}^S \) are as follows [82],

Equation 2.25 \[ \frac{c_{ij}^S}{c_{ij}^T} = \frac{c_{11}^S}{c_{12}^S} = \frac{c_{44}^T}{c_{44}^T} = \frac{C_p}{C_V} \text{ and } c_{44}^S = c_{44}^T \]
where $C_p$ and $C_v$ are heat capacities at constant pressure and constant volume, respectively, which can be estimated from Helmholtz free energy given in Equation 2.18 [66].

### 2.1.5 Lattice force constants matrix

In principle, as an atom in a crystal structure being moved from its equilibrium position, it will generate forces on other atoms. If the displacement is very small, the corresponding response of the system can be assumed to be harmonic, which means the potential energy of the system is actually oscillated around its equilibrium value in quadratic terms based on atomic distance. Basically, the atoms can be thought of as harmonic oscillators chained by atomic bonds. The harmonic interaction between each atom-pair can be regulated by a $3 \times 3$ force constants matrix. For example, the force generated on atom $\alpha$ along the $i$ Cartesian direction by a displacement of atom $\beta$ along the $j$ Cartesian direction can be calculated by [83],

**Equation 2.26**

$$f_{\alpha i}(R') = -\sum_{R,j} D_{\alpha i,j\beta}(R - R')u_{j\beta}$$

where $f$ denotes the force, $\mu$ denotes the displacement and $D_{\alpha i,j\beta}$ denotes the corresponding component of force constants matrix. The vectors in Equation 2.26 represent the positions of the two atoms in lattice. Based on the force constant matrix, we would be able to solve the lattice Green function which is particularly useful for first-principles modeling of dislocations. In the present work, the force constant matrix for BCC W is calculated by the “small displacement method” as built in VASP. A BCC $5 \times 5 \times 5$ supercell comprised of
250 W atoms are used for the calculation. A small displacement has been applied on one atom in the supercell, and then static calculations are performed for computing the forces on each atom. Based on the forces and the displacement, the force constants matrices are derived using PHON [84].

### 2.2 Flexible boundary condition method

Calculating the core structure of an isolated dislocation via first principles (FP) approach is subtle, because the long-field strain induced by the single dislocation is incompatible with periodic boundary conditions imposed in the method. One way to eliminate the long-range stress field is to arrange two dislocations with inverse Burgers vectors in one supercell, which is called dislocation dipole method[85–87]. However, the estimations of Peierls stress via this method is found to be scattered and strongly dependent on supercell size. This results from the dislocation-dislocation interaction and the image stress produced by the boundary conditions[87].

Here, a method so-called the ‘flexible boundary condition’, which is based on the lattice Greens function (LGF) is used to solve the issues mentioned above by modeling an isolated single dislocation[88,89]. The flexible boundary condition method couples the simulation supercell to an infinite bulk by treating an intermediate region away from the dislocation core as harmonic and relaxes the forces from the core atoms by the LGF. As shown in Figure 2.1, the simulation supercell is divided into three regions: core (I), transition (II) and buffer (III). The size of region I is estimated by the partial dislocation
splitting width of the dislocation from the Peierls-Nabarro model[8]. Region II is the intermediate region where the initial forces are small and harmonic. The size of region II is usually at a width of around 2-3 times that of the burgers vector length. Region III act as a buffer to protect the forces in region I and II from the boundaries and the size of it can be estimate from a simulation of a free surface.

Figure 2.1. Schematics of the geometry of the simulation supercell for flexible boundary condition method

The initial atomic positions are approximated by the anisotropic elastic solution [90]. Region I is first relaxed using the Hellmann-Feynman forces from the first-principles calculations. Then, the incompatibility forces, generated for the atoms in region II, are removed by displacing all atoms within the supercell according to the LGF solution,

**Equation 2.27** \( u_{ia} = \sum_{i,\beta} G_{ia,\beta} (R - R') f_{j\beta} \)
where the indices $\alpha, \beta$ denote atoms, and $i,j$ denote the Cartesian components. $u_{i\alpha}$ is the displacement of atom $\alpha$ along the $i$ direction and $f_{j\beta}$ is the Hellmann-Feynman force on atom $\beta$ along the $j$ direction. The atoms in region III are only moved by the corrective displacements of the LGF during the update stage. Relaxations in region I (FP) and region II (LGF) are iterated until forces converge in the two regions.

To perform this relaxation scheme, an efficient numerical calculation for the LGF is necessary. Techniques for calculating LGF numerically for point defects in cubic crystal have been well developed previously [91,92]. Recently, the automated method to calculate the LGF for 1D, 2D and 3D crystalline defects in the Bravais lattice has been developed by Trinkle [62]. The input data for LGF calculation is the elastic constants and force constants matrix of the crystal structure of interest. Then, the method has been expended by Yasi et al. to compute the LGF for the crystal structure of which the primitive cell has more than 1 atom [93]. The calculation details [62] for Bravais lattice are summarized in brief below.

By comparing Equation 2.27 with Equation 2.26, it is easy to see the connections between the force constants matrix and the LGF. However, due to the singularity of the force constant matrix, the LGF and force constants matrix are actually pseudoinverse to each other,

\begin{equation}
\sum_{\mathbf{R}',j} D_{ij} (\mathbf{R} - \mathbf{R}^*) G_{ij} (\mathbf{R}' - \mathbf{R}^*) = \delta_{ij} \delta (\mathbf{R} - \mathbf{R}')
\end{equation}

where the notation of atoms ($\alpha, \beta$) in Equation 2.27 is omitted here since each atom in a Bravais lattice is uniquely corresponds to a lattice coordination vector $\mathbf{R}$. The singularity
of the force constant matrix is due to the absence of forces under a uniform translation of
the crystal, which gives,

**Equation 2.29** \[ \sum_{R,j} D_{ij}(\vec{R}) = 0 \]

Equation 2.29 indicates the force constants matrix has three zero eigenvalues, which makes
it singular. In fact, the computation of LGF is more tractable in reciprocal space. The LGF
and the force constant matrix can be written in reciprocal space as functions of wave vector
in the Brillouin zone by Fourier transformation,

**Equation 2.30** \[ \tilde{G}(\vec{k}) = \sum_R e^{i\vec{k} \cdot \vec{R}} G(\vec{R}) \]

**Equation 2.31** \[ \tilde{D}(\vec{k}) = \sum_R e^{i\vec{k} \cdot \vec{R}} D(\vec{R}) \]

In reciprocal space, Equation 2.28 can be simplified as,

**Equation 2.32** \[ \tilde{G}(\vec{k}) \cdot \tilde{D}(\vec{k}) = I \]

The singularity of the force constant matrix converts to \( \tilde{D}(\vec{k} = 0) = 0 \), which results in a
first-order pole at the gamma point. Expect the gamma point, we have \( \tilde{G}(\vec{k}) = [\tilde{D}(\vec{k})]^{-1} \) for all
other points. In addition, there are also second-order pole and discontinuity at the gamma
point in \( \tilde{G}(\vec{k}) \), which comes from the expansion of \( \tilde{D}(\vec{k}) \) for a small \( k \),

**Equation 2.33** \[ \tilde{D}(\vec{k}) \approx \sum_R D(\vec{R}) \left[ 1 - \frac{1}{2} (\vec{k} \cdot \vec{R})^2 + \frac{1}{24} (\vec{k} \cdot \vec{R})^4 \right] \]

Therefore, to accurately compute the \( \tilde{G}(\vec{k}) \) requires an analytic treatment of the small \( k \)
behavior separated from the rest of the Brillouin zone. Equation 2.33 can be written as two
functions with different orders in \( k \),

**Equation 2.34** \[ k^2 \tilde{X}^{(2)}(\vec{k}) - k^4 \tilde{X}^{(4)}(\vec{k}) \]
where $\hat{k} = \tilde{k}/k$. The first function $\tilde{\Lambda}^{(2)}(\hat{k})$ can be calculated based on the continuum theory,

\textbf{Equation 2.35} \quad \tilde{\Lambda}^{(2)}(\hat{k}) = \frac{1}{k^2} \sum_{m,n} k_m k_n \left\{ \frac{1}{2} D_{ij} (\hat{R}) R_{mn} R_n \right\} = \frac{V}{k^2} \sum_{m,n} k_m C_{mn} k_n = V [\hat{k} C \hat{k}]

where $V$ is the volume of the unit cell and $C_{mn}$ is the tensor component of the forth-rank elastic stiffness tensor, $C$. The second function $\tilde{\Lambda}^{(4)}(\hat{k})$ is related to,

\textbf{Equation 2.36} \quad k^4 \tilde{\Lambda}^{(4)}(\hat{k}) = \sum_{ijmn} k_i k_j k_m k_n \left\{ - \frac{1}{24} D (\hat{R}) R_i R_j R_m R_n \right\}

Therefore, the corresponding LGF for a small $k$ is written as,

\textbf{Equation 2.37} \quad \tilde{G}(\hat{k}) = k^{-2} \left[ \tilde{\Lambda}^{(2)}(\hat{k}) \right]^{-1} + \left[ \tilde{\Lambda}^{(2)}(\hat{k}) \right]^{-1} \tilde{\Lambda}^{(4)}(\hat{k}) \tilde{\Lambda}^{(2)}(\hat{k})^{-1} + O(k^2)

where

\textbf{Equation 2.38} \quad \tilde{G}^E(\hat{k}) \equiv k^{-2} \tilde{\Lambda}^{(2)}(\hat{k})^{-1} = \frac{1}{V k^2} [\hat{k} C \hat{k}]

and

\textbf{Equation 2.39} \quad \tilde{G}^{dr}(\hat{k}) \equiv \left[ \tilde{\Lambda}^{(2)}(\hat{k}) \right]^{-1} \tilde{\Lambda}^{(4)}(\hat{k}) \tilde{\Lambda}^{(2)}(\hat{k})^{-1} + \tilde{G}^E(\hat{k}) \left[ - \frac{1}{24} \sum R D (\hat{R} \cdot \hat{R})^4 \right] \tilde{G}^E(\hat{k})

$\tilde{G}^E$ is actually the Fourier transformation of the elastic Green function, which relates to the second-order pole at the gamma point, while $\tilde{G}^{dr}$ only relies on vector $\tilde{k}$, which gives the discontinuity at the gamma point since $\tilde{G}^{dr}$ does not exist when $k$ reach to zero. We also induce a truncating function to describe the LGF in the entire first Brillouin zone. The truncating function used here is a continuous and differentiable cut-off function, which is written as,
where \( x = k / k_{\text{max}} \) in which \( k_{\text{max}} \) is the radius of a sphere inscribed in the Brillouin zone. Then, the LGF in the first Brillouin zone is written as,

**Equation 2.41**

\[
\tilde{G}(\vec{k}) = \tilde{G}^E(\vec{k})f(k / k_{\text{max}}) + \tilde{G}^{dc}(\vec{k})f(k / k_{\text{max}}) + \left[ \tilde{G}^E(\vec{k}) + \tilde{G}^{dc}(\vec{k}) \right] f(k / k_{\text{max}})
\]

where the term in braces is the semicontinuum function, \( \tilde{G}^{sc} \). Based on this approximation (Equation 2.41), we would be able to re-write the LGF in the Brillouin zone into three pieces: the elastic Green function, the discontinuity correction, and the semicontinuum function. Each of the three pieces will be inverse Fourier transformed to obtain the LGF in the real space. The inverse Fourier transformations of \( \tilde{G}^E \) and \( \tilde{G}^{dc} \) are handled analytically, while \( \tilde{G}^{sc} \) is inverse Fourier transformed using a discrete numerical mesh.

The current derivations of LGF is for a 3D case. The 2D LGF for line defects, such as dislocation, can be obtained by,

**Equation 2.42**

\[
\tilde{G}^{2D} = \sum_{n=-\infty}^{\infty} \tilde{G}^{3D}(\vec{R} + n\vec{t})
\]

where \( \vec{t} \) is a threading lattice vector which gives the periodicity along the dislocation line.
2.3 Nye tensor and dislocation geometry visualization

Burgers vector is the most basic parameter in describing dislocation geometries. It can be more generally defined as the closure failure of a closed circuit path of arbitrary shape and size in the dislocated crystal. However, for the non-planar dislocation, it is hard to be viewed by the Burgers vector circuit. In fact, since the dislocation induced lattice distortion is smooth and continuous, a differential circuit path in a dislocated crystal encloses a non-zero distribution of infinitesimal dislocations; no matter the circuit path includes or precludes the dislocation core. The corresponding infinitesimal Burgers vector is related to the Nye tensor $\alpha$ by [94],

$$d\vec{b} = \alpha \cdot \vec{n} ds$$

where $ds$ is the area of the closed circuit and $\vec{n}$ is normal vector with the area being $ds$.

Therefore, the components of the Nye tensor represents the infinitesimal Burgers vector of the interested directions (edge or screw), which is particularly useful to view the geometry of dislocation structure and analyze dislocation dissociation. The Nye tensor can be obtained by,

$$\alpha = -(\nabla \times G)$$

where $G$ is lattice corresponding tensor, which can be derived based on the finite strain theory [94,95]. In a crystal structure, any lattice vector $d\vec{x}$ in undeformed condition can be related its deformed configuration, $d\vec{x}'$, via its lattice correspondence tensor $G$,

$$d\vec{x} = d\vec{x}' G$$

As shown in Figure 2.2a, the relative position of every atom $i$ in a perfect crystal could be defined as a set of nearest neighbor vectors, $P^{(n)}$, which is:
Equation 2.46 \[ P_i^{(n)} = (\vec{p}_{i1}, \vec{p}_{i2}, \ldots, \vec{p}_{ij}, \ldots, \vec{p}_m) \]

where \( n \) is the number of nearest neighbors which is 8 for BCC crystal. After lattice distortion, the nearest neighbor vectors of atom \( i \) may be deformed. We use a set \( Q^{(n')} \) to describe the relative position of atom \( i \) in a deformed state,

Equation 2.47 \[ Q_i^{(n')} = (\vec{p}_{i1}, \vec{p}_{i2}, \ldots, \vec{p}_{ij}, \ldots, \vec{p}_{in}) \]

For example, if atom \( j \) moved to \( j' \) after deformation, the nearest neighbor vector \( \vec{p}_{ij} \) will be \( \vec{q}_{ij'} \) in the deformed crystal. (Figure 2.2b)

**Figure 2.2** (a) Nearest neighbor vector \( \vec{p}_{ij} \) in the undeformed BCC lattice; (b) nearest neighbor vector \( \vec{q}_{ij'} \) after deformation

As a result, the corresponding lattice tensor can be calculated via a mean-squares solutions as [94,95],

Equation 2.48 \[ G = (Q^T \cdot Q)^{-1} \cdot Q^T P \]

For crystal under complex deformation, i.e., strain induced by dislocation or grain boundaries, the nearest neighbor vectors may be extremely distorted and its number will also change. In this case, we compute the angles \( |\Phi_{pq}| \) between the deformed vector \( \vec{q}_{ij'} \)
and all reference vectors $P^{(n)}$. The reference vector $\tilde{p}_{ij}$ with the smallest angular difference will be the one undeformed corresponding vector to $\tilde{q}_{ij}$ [94,95]. The tolerance of the vector angles is set as $30^\circ$ degree for the dislocation calculations in the present dissertation.
Chapter 3

Effects of Alloying Elements and Temperature on the Elastic Properties of W-based Alloys

3.1 Introduction

Although first-principles approaches based on density functional theory have been proven to be a reliable and efficient method in predicting elastic properties of various alloying systems [61,79,96–98], little work has been performed on the elastic properties of W and its alloys in a comprehensive manner, especially at finite temperatures. Through first-principles calculations, the present work aims to close this gap in understanding by investigating systematically the effects of alloying elements on the elastic properties of BCC W, as a function of temperature, including isothermal and isentropic elastic stiffness components, bulk modulus, shear moduli, Young’s modulus, and elastic anisotropy. Nineteen transition metal alloying elements are considered: Ti, V, Cr, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. In addition, the trends, regularities of the predicted elastic properties, and their electronic origins are discussed.
3.2 Computational details

First-principles elastic stiffness constants of a series of W-1.85 at.% X solid solutions are calculated by using the Vienna Ab-initio Simulation Package (VASP) [57]. A BCC $3\times3\times3$ supercell comprised of 53 W atoms and one additional atom associated with alloying element X is used. Further, the projector augmented wave method (PAW) [99] and the exchange-correlation functional depicted by the generalized gradient approximation (GGA-PW91) are employed [75]. The energy cutoff of the plane wave is set as 350 eV. For all the calculations, the supercells are relaxed by the Methfessel-Paxton method [100]. The Brillouin-zone integration is performed by using a tetrahedron method with Blöchl corrections [101] and a Monkhorst-Pack $k$-points grid of $8\times8\times8$ [100]. The energy convergence criterion of the electronic self-consistency is set as $10^{-6}$ eV/atom for all of the calculations. The contour plots of the differential charge density are generated using VESTA [102,103]. The details of deriving elastic constants from the first-principles outputs were discussed in Chapter 2.

3.3 Results and discussion

In this section, we first report the regularities of elastic properties and their electronic origins for the specific W-X alloys at 0 K (Sec. 3.3.1). Second, we present the elasticity of the W-X alloys at finite temperatures (Sec. 3.3.2).
3.3.1 Elastic Properties at 0 K

Table 3.1 summarizes the calculated elastic properties of the W-X alloys at 0 K as well as the equilibrium volumes and lattice parameters predicted by the EOS fitting. It is found that the present prediction of equilibrium volume of BCC W agrees well with experimental data and previous calculations [61,104]. For the elastic stiffness components, the present $c_{11}$ and $c_{12}$ values are in good agreement with the experimental data at 4.2 K [104], with the largest difference less than 6% for $c_{12}$. The calculated $c_{44}$ value in the present work has a 12% deviation compared to the experimental data, but it agrees well with a previous calculation [61].

To investigate the lattice distortion induced by the solute atoms, Figure 3.1 plots the EOS predicted equilibrium volumes from Table 3.1 compared to the values calculated based on Vegard’s law for pure elements with a BCC structure [61]. It is shown that the effect of X on the volume of the dilute W-X alloys can be represented as a mechanical intermixing for the alloying elements which have atomic volumes close to BCC W. Deviation between the first-principles calculation and the prediction from Vegard’s law is found when the alloying element has a large disparity of its atomic volume compared to that of BCC W. On one hand, smaller alloying elements lead to positive deviations, such as those of Ni and Co. On the other hand, large negative deviations are found for alloying elements Y, Zr, and Hf, which all have much larger atomic volumes than BCC W. The large deviations from Vegard’s law indicate that strong interactions exist between these solute elements and W, in addition to the mechanical mixing between them. Such
interactions can be ascribed to the change of the local electronic environment of the solute atom when it is substituted for a W atom in the BCC W matrix [105].

For dilute solid solutions, the changes of lattice parameter can be approximated as a linear function of alloying concentration [106],

**Equation 3.1** \[ a_{W_{x},X} = a_{W_{x}} + k_{X} x_{X} \]

where \( a_{W_{x},X} \) and \( a_{W_{x}} \) are the lattice parameters of the W-X solutions and pure W, respectively, \( x_{X} \) is the mole fraction of alloying elements, and \( k_{X} \) is defined as a linear regression coefficient for element X. Calculated lattice parameters of the W-X solutions and the corresponding linear regression coefficients are listed in Table 3.1. Figure 3.2 plots the linear regression coefficients vs. the lattice parameters of alloying elements with the BCC crystal structure. Available experimental values, obtained by a fitting of experimental lattice parameters [107,108], are also included, showing a good agreement. It is found that the linear regression coefficients are generally proportional to the lattice parameters of the alloying elements in the BCC structure. However, Ti and Y are slightly off the observed trend.

To illustrate the effect of alloying elements on the elastic modulus of BCC W, Figure 3.3 displays the calculated bulk moduli and compares them to those obtained from a linear combination of the pure elemental moduli in the BCC structure in terms of their mole fractions. For most alloying elements studied, it is found that the bulk modulus of the W-X dilute alloy can be approximated as a mechanical mixing of the bulk moduli of X and W. However, similar to the volume analysis described in Figure 3.1, deviations from this trend are observed for Y, Zr, and Hf, scaling with their respective atomic numbers, which,
by the way, all have the HCP structure and possess fewer valence electrons than W. However, it is noted that no clear correlation is found between the shear moduli of the W-X dilute alloys and those of the pure alloying elements with a BCC structure.

Previously, it has been shown that elastic moduli are generally correlated to equilibrium volume [61,79,97]. Therefore, the calculated polycrystalline bulk and shear moduli of the W_{53}X alloys are plotted as a function of the equilibrium volume of alloys in Figure 3.4a and 3.4b. As seen in Figure 3.4a, the alloys with smaller equilibrium volumes have larger bulk moduli. In addition, within each group of 3d, 4d, and 5d alloying elements, it is found that the bulk modulus of W_{53}X decreases linearly with increasing equilibrium volume. Such trend was also reported for Ni- and Mg-based alloys [79,97]. Other than that for the bulk modulus, no clear correlation can be found between shear modulus and equilibrium volume, as is shown in Figure 3.4b. It is observed that all of the alloying elements decrease the shear modulus of BCC W to some extent. More precisely, the alloying effects on the shear modulus are found to correlate with the number of the valence electrons of the alloying elements, as shown in Figure 3.5. For the alloying elements of Cr and Mo with the same numbers of valence electrons as W, the reductions of shear modulus are not significant compared to the other alloying elements. For the elements containing 3 and 5 electrons in their d orbital, respectively, such as V, Nb, Ta, Fe, Ru, and Os, the effect of alloying on shear modulus is moderate. As the disparity of the number of the valence electrons between the alloying element and W becomes larger, the shear modulus of BCC W decreases further. For example, there is a significant decrease of the shear modulus of BCC W alloying with Y, Zr, and Pd. A similar trend is also observed for the shear modulus along the <111> direction ($G_{111}$). Since valence electrons are crucial to the formation of
chemical bonds, this trend implies that alloying effects on the shear modulus of W can be understood in terms of the interatomic bonds between the W and the solute atoms. Detailed discussion is provided in a later paragraph.

The elastic deformation behavior of crystalline materials originates from the stretching of atomic bonds when a force is applied. For example, the bulk modulus, which represents the compressibility of a crystal under hydrostatic pressure, is generally related to the stiffness of the chemical bonds. Therefore, it is interesting and important to investigate the electronic origins further, more particularly, how the elastic properties of the W-X alloys are changing. According to Miedema et al. and Li and Wu, (see references [109,110]), for pure alkali metals and non-transition metals, \( \sqrt{B/V_m} \) is linearly proportional to the electron density at the boundary of the Wigner-Seitz cell, where \( B \) is the bulk modulus and \( V_m \) is the molar volume of the element. The electron density at the boundary of the Wigner-Seitz cell, \( n \), can be calculated via \( n = Z_B / V \), where \( Z_B \) is the bond valence of the element and \( V \) is the atomic equilibrium volume at 0 K. This linear relationship has been validated for Ni-based alloys by taking into account the effect of alloying elements on \( n \) [96]. Here, in a similar manner, we compute \( n \) for W_{55}X based on a linear combination of the constituent elements, similar to Vegard’s law,

\[
\frac{n_{W_{55}X}}{n_{W_{55}X}} = \left( \frac{53}{54} n_W V + \frac{1}{54} n_X V \right) / V_{W_{55}X}
\]

where the electron densities, \( n_W \) and \( n_X \), are calculated from equilibrium volume[5] and bond valence data[34] of the pure elements found in published literature. Figure 3.6 shows that a linear relationship between \( \sqrt{B/V_m} \) and electron density \( n \) is obeyed in dilute W-based
alloys. It is found that the bulk modulus of $W_{53}X$ is positively proportional to the electron density, $n_{W_{53}X}$. In fact, the value of $n$ reflects how dense the electron gas of a metallic system is. This is because the bond valence ($Z_B$) is defined as the number of participating electrons where each atom contributes to the electron gas[111]. Thus, a higher electron density $n$ indicates a denser electron gas, implying stiffer chemical bonds between the atoms[112]. Therefore, the $W_{53}X$ alloys with a higher electron density, $n$, are anticipated to have stiffer chemical bonds between atoms, which, in turn, would result in a larger bulk modulus.

The influence of alloying elements on the shear modulus along the [111] direction of W can be better understood in terms of the differential charge densities that can be represented by the charge density difference for the calculated structure with and without the self-consistent calculations. Figure 3.7a, 3.7b, 3.7c, and 3.7d show the differential charge density plots in the (1̅10)-plane of $W_{53}X$ (with $X=W, Mo, Ti, and Pd$) revealing the bonding environments between nearest neighbors. The relative intensity and directionality of the differential charge density are illustrated by a combination of color mapping and contour plotting. As seen from Figure 3.7a, the charge density of pure W is higher between adjacent atoms in the (1̅10) plane along the <111> directions; note, this distance (dashed arrow in Figure 3.7a) is the shortest distance between two W atoms. This implies that the interatomic bonds along the <111> directions in pure W are stronger than any other directions. As a result, the shear modulus along the <111> directions are expected to be larger than that associated with a polycrystalline microstructure (Table 3.1). Instead, from a polycrystalline microstructure, an average of shear moduli sampled from all
directions would be expected. Furthermore, as seen from Figure 3.7c and 3.7d, the W-X bonds for W-Ti and W-Pd along the <111> directions are distorted and weaker than the W-W bonds. Correspondingly, the shear moduli $G_{111}$ of $W_{53}$Ti and $W_{53}$Pd are much lower than that of pure W (Table 3.1). By analogy, the change of $G_{111}$ caused by the alloying element Mo is relatively small; this can be attributed to the fact that W-Mo bonds are very similar in nature to W-W type bonds (Figure 3.7b). Note, the crystal structures of Mo and W are isomorphous and they have similar atomic radii.

The observed decrease of the elastic shear moduli can be interpreted as a form of lattice softening induced by the alloying elements. Usually, it is considered that lattice softened alloys would lead to and may exhibit good plasticity due to the change of elasticity and crystal stability [5–7]. For example, the ideal shear strength in BCC crystals is governed by the shear modulus along the <111> directions, $G_{111}$ [5]. As $G_{111}$ decreases, the crystal lattice is expected to be softer or more deformable in response to a shear stress. Based on the Peierls-Nabarro model, the size of the dislocation glide barrier is also proportional to the shear modulus along the Burger’s vector [8]. This implies that the glide of a $\frac{1}{2}<111>$ screw dislocation in BCC W could be promoted as the $G_{111}$ decreases. Therefore, it is conceivable that the lattice softening induced by alloying elements may also result in a preferential softening for plastic deformation in a practical sense as well. Experimentally, Re has been recognized to strongly soften BCC W at room temperature, however, with alloying contents of over 5 at.% [1,3,9]. In addition to Re, Ru, Os, or Ir have been reported to also have obvious softening effects on BCC W, but at much lower alloying levels (1~2 at.%) [3]. It is interesting to note that at very a low alloying concentration (1.85 at.%), the effect of Re on lattice softening (i.e., a decrease of $G_{111}$) is weaker compared to
the effects of Ru, Os and Ir, as shown by the present calculations (Table 3.1). However, the lattice softening induced by Re becomes much more significant as at concentrations greater than 5 at.% [98]. As mentioned above, the alloying elements that have large disparities of the number of valence electrons compared to pure W will lead to significant decrease of $G_{\text{111}}$. Therefore, by taking the real solubility limits of alloy elements in BCC W into account, it is hypothesized that Ti, Rh, and Hf could be possibly more promising candidates to soften BCC W via alloying. Nevertheless, it needs to be pointed out that this hypothesis is purely based on the elastic properties of the host metal and alloying additions which may not be able to reflect the overall effects of alloying on plasticity. Further calculations incorporating a better plasticity model were performed to validate the current hypothesis, which will be discussed in more detail in the later chapter.

### 3.3.2 Elastic properties at finite temperatures

The elastic properties of pure W and W$_{53}$X type alloys at finite temperatures are predicted via the quasi-static approach based on the Debye model presented in Section 2.2. The Debye temperature of pure W is calculated to be 363 K in the present work, which is in good agreement with the experimental value (378 K) and results of a previous calculation (366 K) [65]. Figure 3.8 plots the predicted isentropic and isothermal $c_{ij}$’s and the bulk modulus of pure W from 0 to 3750 K. Available experimental data, measured in the isentropic condition, are also included for comparison [78,104,113]. It is shown that the predicted elastic constant values decrease with increasing temperature. This is caused by lattice expansion at high temperatures which leads to the weakening of atomic bonds.
Computed values of the isothermal bulk modulus and $c_{44}$ agree more closely with the experimental data. A relatively large discrepancy is observed between experimental $c_{11}$ and the predicted values at high temperatures. This is possibly due to the strong anharmonicity in W at high temperatures or caused by the thermal stress fluctuations, which are not considered in the present work.

Table 3.2 summarizes the predicted isothermal and isentropic elastic constants of W$_{53}$X at several selected temperatures, 300, 900, 1500, 2100, 2700, and 3300 K. It is worth mentioning that the value for the isothermal $c_{44}$ equals to the isentropic $c_{44}$ for a cubic crystal. Similarly to pure W, the predicted $c_{ij}$ values of W$_{53}$X decrease with increasing temperature. For the sake of applicability, the predicted $c_{ij}$ values of W$_{53}$X from 300 to 3750 K are fitted to a polynomial function [79],

**Equation 3.3**

$$c_{ij}(T) = a_0 + a_1 T + a_2 T^2$$

where $a_0$, $a_1$, and $a_2$ are fitting parameters. The fitting parameters obtained for each W$_{53}$X are listed in Table 3.2. In addition, fitting errors are estimated by,

**Equation 3.4**

$$\text{Error} = \sqrt{\frac{\sum (c_{fit} - c_{calc})^2}{n c_{calc}}}$$

where $c_{calc}$ and $c_{fit}$ are elastic stiffness constants predicted by the quasi-static approach and by Equation 3.3, respectively. These fitting errors are also included in Table 3.2. As seen in Table 3.2, the decreasing trend of elastic constants is indicated by $a_1$ roughly. The average values of $a_1$ for isothermal $c_{11}$, $c_{12}$ and $c_{44}$ are $-2.88 \times 10^{-2}$, $-1.60 \times 10^{-2}$ and
\(-0.58 \times 10^{-2}\) GPa/K, respectively. For isentropic \(c_{11}\) and \(c_{12}\), the average values of \(a_I\) are 
\(-1.65 \times 10^{-2}\) and 
\(-0.56 \times 10^{-2}\), respectively.

### 3.4 Conclusion

In this part of the dissertation, the effects of alloying elements and temperature on the elastic properties of BCC W, including isothermal and isentropic elastic stiffness constants, bulk modulus, shear modulus, Young’s modulus and elastic anisotropy have been studied systematically via first-principles calculations. Nineteen transition metal alloying elements (X’s) have been considered: Ti, V, Cr, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. Based on the first-principles results at 0 K, the alloying effects on the elasticity of BCC W can be summarized as follows: (i) the bulk modulus of the dilute W-X alloys decreases with increasing equilibrium volume, particularly for alloying elements in the same period; (ii) all alloying elements decrease the shear modulus of BCC W to some extent; (iii) the earlier or later transition elements (e.g., Y, Zr and Pd) have stronger effects on the shear modulus than the other elements (e.g., Cr and Mo) which have the same number of valence electrons as W; and (iv) the largest decrease of elastic properties of W is due to the alloying element Y. In addition, effects of alloying elements on the elastic properties of W, such as the bulk modulus and shear modulus, are traceable from the redistribution of electronic charge densities caused by alloying elements. At finite temperatures, the isothermal and isentropic elastic stiffness components of the W-X dilute alloys are predicted via a quasi-static approach based on the Debye model and show a
decreasing trend of elasticity with increasing temperature due to lattice expansion at finite temperatures. Computed elastic properties are compared to available experimental data and are found to be in good agreement.
Table 3.1 Calculated elastic properties of W$_{53}$X alloys at 0 K, including elastic stiffness constants ($c_{ij}$’s), Young’s modulus (E), bulk modulus (B), and shear modulus (G) from the Voigt approach, shear modulus along the [111] direction ($G_{111}$), and the universal elastic anisotropy ratio ($A^U$). The unit for each elastic property is GPa. The EOS predicted equilibrium volume ($V_0$ ($\text{Å}^3$/atom)), the corresponding lattice parameter ($a_0$ (Å)), and lattice regression coefficient ($k_x$) are shown as well. For BCC W, available experimental data and previous calculations are also included for comparison.

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Table 3.2 Predicted isothermal elastic stiffness constant ($c_{ij}^T$) and isentropic elastic stiffness constant ($c_{ij}^S$) of W$_{53}$X at 300, 900, 1500, 2100, 2700, and 3300 K. The unit for the elastic stiffness constants is GPa. The polynomial fitting parameters and fitting errors are also included; their values are based on the predicted elastic data from 300 to 3300 K.

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Figure 3.1 Calculated equilibrium volumes of the W$_{53}$X alloys (listed in Table 3.1) compared to the predictions from Vegard’s law of pure elements with a BCC structure [61]. The dashed line indicates where the two methods produce the same result.
**Figure 3.2** Calculated lattice regression coefficients ($k_x$) of the W$_{53}$X alloys (see Equation 3.1) vs. lattice parameters of the alloying elements (Xs) in the BCC structure [61]. The $k_x$ values fitted from experimental data are labeled as black dots [107,108].
Figure 3.3 Bulk modulus of the W₅₃X alloys (listed in Table 3.1) compared to the predictions from a linear combination of bulk moduli of the pure elements in the BCC structure in terms of their mole fractions [61]. The dashed line indicates where the two methods agree.
**Figure 3.4** Calculated bulk and shear moduli of the W$_{53}$X alloys based on the Voigt approach as a function of the equilibrium volume; (a) bulk modulus and (b) shear modulus.
**Figure 3.5** Calculated shear moduli of the W_{53}X alloys with respect to the number of the valence electrons of the alloying elements.
Figure 3.6 Correlation between $n$ and $\sqrt{B/V_m}$ for the W$_{53}$X alloys.
Figure 3.7 Differential charge densities of pure BCC W and the W$_{53}$X alloys in the (1 $\bar{1}$ 0) plane; (a) pure BCC W, (b) W$_{53}$Mo, (c) W$_{53}$Ti, and (d) W$_{53}$Pd. The shortest distance between two W atoms or the solute and W atom is shown by dashed arrows. Note, the lattice indices in the figures are with respect to the 54-atom supercell. The unit of charge density is e/Å$^3$. Contour lines are spaced at 0.002 e/Å$^3$. 

![Figure 3.7](image)
Figure 3.8 Predicted isentropic and isothermal $c_{ij}$ values of pure W from 0 to 3750 K. Available experimental data are also included for comparison ([104], [78], [113]).
Chapter 4

Solutes Induced Solid-Solution Softening and Hardening in BCC W

4.1 Introduction

Recently, benefitting from the development of computational materials science, the mechanism of the SSS phenomenon has been further studied via the DFT based first-principles calculations. For instance, the electronic origin of the SSS effects on Mo and W has been investigated in the case of 5d transition elements via first-principles calculations of generalized stacking fault energy [114–116]. It is found that the promotion of the dislocation mobility at the solute sites is due to local chemical bond weakening induced by solute atoms [114]. On the other hand, it is demonstrated by the virtual crystal approximation (VCA) based DFT calculations that Re-induced ductilization in BCC W is also caused by a change in the preferred slip planes when the Re concentration is larger than 25 at.% [85,87]. Similar work has been done to investigate the effects of some individual elements on the Peierls barriers of BCC W [98]. These works have succeeded in qualitatively explaining the softening, and so as the ductilization effects of individual solute elements on the BCC W. However, the solute induced SSS phenomenon has been
experimentally demonstrated to be very sensitive to the solute concentration [9,15]. For example, the yield strength minimum of W-Re alloys was found at the Re concentration about 7 at.% [15]. Correspondingly, the tensile failure strain also reached maximum value. As the Re concentration increased over 7 at.%, a yield strength hardening behavior has been observed instead of further softening. Meanwhile, a decrease of ductility was also observed [15]. Therefore, for the purpose of improving the low temperature ductility of W-based alloys, a quantitative prediction is required to determine the optimal alloying concentration at which the SSS effect is maximized. Close study has been performed in BCC Mo [19]. It is shown that the softening and hardening effects of Re and Pt on BCC Mo can be quantitatively predicted over a range of concentrations and temperatures via integrating the first-principles calculations of the solute-dislocation interactions with an improved mesoscopic solid-solution softening model [19]. Due to the similarity between Mo and W, it is possible to study the SSS behavior in the W-based alloys in the same way.

In this part of the dissertation, the solute-induced softening and hardening in BCC W is systematically studied for twenty-one substitutional alloying elements, namely Al, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt, to search possible substitutes for Re that will result in a similar softening effect in W. The changes in the energy barrier and stress scale of dislocation motion from the solute-dislocation interactions are directly computed via first-principles approaches with special dislocation boundary conditions [19,20,89,117]. The solute effects on critical resolved shear stress of the $\frac{1}{2} <111>$ screw dislocation in BCC W at room temperature are quantitatively predicted, as a function of alloy concentration, via an improved mesoscopic solid-solution model [19] by using the first-principles results as input parameters. Based on the predictions, Al and
Mn are proposed to be promising substitutes for Re, which are found to introduce a similar softening effect as Re in BCC W. In addition, the trends, regularities of the solute-dislocation interactions, and their correlations to the core structure geometries are discussed.

4.2 Computational details

To accurately compute the interactions of the solutes with the screw dislocation in BCC W, we use DFT with flexible boundary condition for a stress-free dislocation core structure. The DFT calculations are performed using the Vienna ab-initio simulation package (VASP) [57]. A plane-wave basis with the projected-augmented wave (PAW) method [99] and ultrasoft pseudopotentials [58] are employed. The electronic exchange-correlation effects are depicted by the generalized gradient approximation [75]. The energy cutoff of the plane wave is set as 250 eV with a Monkhorst-Pack k-points grid of 1×1×8 to ensure an accurate treatment of the potentials [100]. The energy convergence criterion of the electronic self-consistency is set as 10^{-7} eV/atom for all of the calculations. The structure relaxation is terminated until the maximum force acting on the atoms becomes less than 5 meV/Å. With these setting parameters, the lattice constant of bulk BCC W is calculated to be 3.172 Å, in a good agreement with experimental data and previous calculations [67].

A single \( \frac{1}{2} <111> \) screw-character dislocation is placed in the center of a periodic supercell which has a size of \( 5[11\bar{2}] \times 9[\bar{1}10] \times [111] \) in terms of the BCC lattice index. The supercell contains 540 atoms and repeats for two Burgers vector lengths along the
dislocation line direction. The supercell geometry is chosen to guarantee that the nearest-neighbor distance for atoms across the supercell boundaries is close to the bulk nearest-neighbor distance to minimize the overlap of atomic charge densities in the supercell boundaries. The initial geometry of the dislocation is obtained by displacing the atoms according to the integral formulation of the anisotropic elastic displacement field [90]. The supercell is then relaxed via first-principles calculations integrated with the flexible boundary condition method [19,20,89]. The relaxation scheme consists two parts: the DFT relaxation of atoms in the dislocation core region and the lattice Green function (LGF) relaxation of the atoms outside the core region. To do this, the atoms in the cell are separated into three regions based on their planar distance from the dislocation core, as shown in Figure 4.1. The region I contains 120 atoms (marked as yellow in Figure 4.1) with distances less than 10.5 Å from the core. The region II contains 162 atoms (marked as blue in Figure 4.1) between 10.5 Å and 16 Å, and the region III are the remaining 258 atoms which serves as a buffer region between periodic images of region II atoms. First, the atoms in region I are relaxed via DFT approaches using ab initio forces while the atoms in region II and III are fixed. The resulted displacements in region I generated forces on the atoms in region II and III. Then, the LGF is used to relax the atomic forces in region II by adjusting the positions of all the atoms in region I, II and III. The displacement field of atoms is calculated by:

\[ u_{i\alpha} = \sum_{i,j} G_{i\alpha,j\beta} (\vec{R} - \vec{R}') f_{j\beta} \]

where the indices \(\alpha, \beta\) denote atoms, and \(i,j\) denote the Cartesian components. \(u_{i\alpha}\) is the displacement of atom \(\alpha\) along the \(i\) direction and \(f_{j\beta}\) is the Hellmann-Feynman force on
atom $\beta$ along the $j$ direction. For a given crystal structure (BCC W here), the LGF component, $G_{ia,j\beta}(\vec{R} - \vec{R}')$, is derived from the force constants matrix of the pure BCC W. Detailed derivations are described in Chapter 2. The relaxation cycle iterates until the atomic forces in both region I and II are reduced less than 5 meV/Å. The final relaxed geometry represents the core geometry of a single isolated screw dislocation in BCC W under a stress-free condition.

Once the geometry of the pure W screw dislocation is optimized, individual W atoms in the dislocation core are replaced by solute atoms to compute the solute-dislocation interactions. The interaction energy ($E_{int}$) is defined to be the difference between the energy of the solute in the dislocation core and the reference state where the solute is placed at site far from the dislocation, corresponding to a distance of 2.88$b$. For the solute calculations, only atoms in the region I are relaxed until the forces are less than 5 meV/Å. The LGF relaxation is not performed so that the contributions to the total energy of the configurations from the atoms in region II and III do not change for each solute position. This treatment has been usually used in the dislocation-solute interaction calculations to avoid any ambiguity in the contribution from the long range elastic field to the total energy [89]. Due to the supercell geometry, the solute is periodically repeated every two Burgers vector length ($\sim 5.49$ Å) along the dislocation line direction, which is assumed to have very small effects on the solute-dislocation interaction energy as proved in the Mo system [19]. In fact, since the interaction energy is defined to be the difference between energies of solute in dislocation core site and the reference site, the effect of the solute-solute interaction on the interaction energy can be approximately removed by taking this energy difference. For
solute elements which have spin polarization at their steady state, first-principles calculations with collinear spin alignments are performed for a $W_{33}X$ (X= to Cr, Mn, Co, Fe and Ni) BCC $3 \times 3 \times 3$ supercell to investigate the spin state of these solutes in BCC W at dilute concentration. It is found that the magnetic moment of these solutes are negligibly small. Therefore, in the present work, we perform the solute-dislocation DFT calculations under non-spin polarization condition.

### 4.3 Solid-solution model

The effects of solutes on the flow stress of BCC W can be estimated via the solid-solution model which is given by Sato et.al and Arsenault et. al. previously [8,16,17] and modified by D. Trinkle [19]. At low temperatures, the plastic deformation in BCC refractory metals is controlled by the thermally activated motion of the long-straight $\frac{1}{2}<111>$ screw dislocations [8,16,118]. Firstly, the dislocation moves perpendicular to its line direction to nuclear a pair of opposite-directed “kinks” (i.e., double-kink), as shown in Figure 4.2a schematically. Then, the kinds migrate away from each other along the dislocation line direction, which moves the whole dislocation line forward to the adjacent lattice site (Figure 4.2b). The applied flow stress ($\sigma$) decreases the enthalpy barriers of the double-kink nucleation or kink migration [8,16,118]. In general, the flow stress is measured against applied strain (ε) at a constant strain rate ($\dot{\varepsilon}$) experimentally. $\dot{\varepsilon}$ can be connected to the dislocation motion velocity via the Orowan equation [119],

Equation 4.2

$$\dot{\varepsilon} = b \rho_m \bar{v}_{dis}(\sigma)$$
where $b$ is the length of the Burgers vector, $\rho_m$ is mobile dislocation density and $\bar{v}_{\text{dis}}(\sigma)$ is the average motion velocity of dislocations with stress. In BCC W, the $\frac{1}{2} <111>$ screw dislocation glides on the $\{110\}$ plane. As the kink moves, the dislocation is translated by a distance of $0.94b$, thus $\bar{v}_{\text{dis}}(\sigma) = 0.94b / \bar{t}_{\text{dis}}(\sigma)$. The average time $\bar{t}_{\text{dis}}(\sigma)$ of the dislocation motion is actually the sum of the time taking for double-kink nucleation and kink migration. Therefore, the strain rate actually can be connected with the rates of double-kink nucleation ($\Omega_{dk}$) and kink migration ($\Omega_{km}$).

**Equation 4.3**

$$\dot{\varepsilon} = 0.94b^2 \rho_m \times \left[\Omega_{dk}(\sigma) + \Omega_{km}(\sigma)\right]$$

Since the dislocation motion is thermally activated, both $\Omega_{dk}$ and $\Omega_{km}$ could be written in the form of the Arrhenius equation. The enthalpy barrier of double-kink nucleation with stress in pure W (without solute) is expressed as [8],

**Equation 4.4**

$$\Delta H_{dk}(\sigma) = \Delta H_{dk}^0 \left[1 - \left(\frac{\sigma}{\tau_{dk}}\right)^m\right]^n$$

where $\Delta H_{dk}^0$ is enthalpy barrier at zero stress and $\tau_{dk}$ is the yield stress at zero temperature. In the present work, the exponent parameters $n$ and $m$ use the values of 0.75 and 1.17, respectively, which have been obtained from the fitting of experimental measurements of Ta [120]. For the pure W, the kink-migration is assumed to be much faster than the double-kink nucleation. Therefore, by only considering the double-kink nucleation, Equation 4.3 is expressed as,
\textbf{Equation 4.5} \[ \dot{\varepsilon} = 0.94b^2 \rho_m v_{dk} \exp \left\{ -\frac{\Delta H_{dk}^0}{k_B T} \left[ 1 - \left( \frac{\sigma}{\tau_{dk}} \right)^{0.75} \right]^{1.17} \right\} \]

where \( v_{dk} \) is the prefactor of the nucleation rate. Based on Equation 4.5, the yield stress is derived as a function of temperature,

\textbf{Equation 4.6} \[ \sigma(T) = \tau_{dk} \left[ 1 - \left( \frac{T}{T_{dk}} \right)^{1/1.17} \right]^{1/0.75} \]

where \( T_{dk} \) is,

\textbf{Equation 4.7} \[ T_{dk} = \frac{\Delta H_{dk}^0}{k_B} \left[ \ln v_{dk} - \ln \left( \frac{\dot{\varepsilon}}{0.94b^2 \rho_m} \right) \right]^{-1} \]

Brunner has measured the critical resolved shear stress (CRSS) of single crystal BCC W as a function of temperature under a constant strain rate of \( 8.5 \times 10^{-4} \text{ s}^{-1} \) [121]. Fitting his data to Equation 4.6 we have \( T_{dk} = 818 \text{ K} \) and \( \tau_{dk} = 4.926 \times 10^{-3} \mu \), where \( \mu = 163 \text{ GPa} \) is shear modules of pure W. Using elasticity theory, Argon parametrized \( \tau_{dk} \) and \( \Delta H_{dk}^0 \) in terms of a single parameter \( \alpha \) [8],

\textbf{Equation 4.8} \[ \tau_{dk} = \frac{\pi \mu \alpha}{0.94} \quad \Delta H_{dk}^0 = \frac{\pi}{4} 0.94 \mu b^3 \kappa^{1/2} \]

Based on the fitting results of Equation 4.7, we find \( \alpha = 1.474 \times 10^{-3} \), \( v_{dk} = 3.93 \times 10^{10} \text{ s}^{-1} \) and \( \Delta H_{dk}^0 = 1.107 \text{ eV} \). In addition, based on elasticity theory [8], we are able to calculate the kink width (distance along the dislocation line from start to finish),
Equation 4.9 \[ W_k = 0.94b \frac{1}{2} \alpha^{-1/2} \]

For W, this gives the dislocation width, \( W_k \approx 12b \).

It is believed that the solutes have effects on the maximum value of both the enthalpy barriers of kink nucleation and migration \([8,19,20]\). In addition, the stress dependence of these barriers is also affected by the solutes \([19]\). Based on Trinkle’s model \([19]\), the Peierls stress under alloyed condition, \( \tau_{d\bar{b}}(c) \), could be scaled in terms of the solute concentration, \( c \), and a parameter so-called Peierls misfit, \( \tau' \).

Equation 4.10
\[ \tau_{d\bar{b}}(c) = \tau_{d\bar{b}}(1 + c \tau') \]

Based on Equation 4.8, the enthalpy barrier of double-kink nucleation is scaled as \( \Delta H^0_{d\bar{b}}(c) = \Delta H^0_{d\bar{b}}(1 + c \tau')^{1/2} \). On the other hand, the Peierls stress is correlated to the stiffness for initializing a single atomic row in the dislocation core moving alone the dislocation line direction. Therefore, the Peierls misfits can be directly calculated from the change in the stiffness when a solute doped atomic row is moved \([19]\). As mentioned in section 2.1, a single solute atom is placed in an atomic row in the core of dislocation with periodic repeat distance of two Burgers vector length. Once the doped core is relaxed, the atomic row is displaced incrementally along the dislocation line, and total energy is computed via first-principle approach. The displacement of one single step is 1/48 of Burgers vector length. The energy of the initial relaxed core is used as the reference to be subtracted to give the changes in energy due to the displacement. Four-step displacements are performed in the present work and enough for obtaining the stiffness. In order to estimate the contribution
from the solute atom on the line only, the displacement energy for a pure W dislocation calculated using a periodic repeat distance of one Burgers vector is subtracted,

**Equation 4.11**

\[ \delta E(X) = (E_{X+W}(X,W,\text{disp.}) - E_{X+W}(X,W,\text{relax.})) - (E_{1W}(W,\text{disp.}) - E_{1W}(W,\text{relax.})) \]

where \( \delta E(X) \) is the displacement energy per solute atom (X) long the dislocation line. 

\( E_{X+W} \) denotes the energy of the dislocations structure with one solute atom in the atomic row, and \( E_{1W} \) denotes the energy of the pure W dislocation structure, which is calculated using a periodic repeat distance of one Burgers vector. Apparently, \( \delta E(X) \) approaches zero quadratically as a function of displacement for all solutes. Therefore, the Peierls misfit, \( \tau' \), can be calculated from the difference in the curvature of \( \delta E(X) \) at zero displacement,

**Equation 4.12**

\[ \tau' = \tau^{-1} \frac{d \tau}{dc} = \frac{\text{Curvature}(\delta E(X))}{\text{Curvature}(\delta E(W))} - 1 \]

Due to the interaction between the solute and dislocation, the bonding environment of the double-kink nucleation site is changed. To handle this solute effects, Trinkle et. al. gives a total double-kink nucleation rate with a solute concentration \( c \) as [19],

**Equation 4.13**

\[ \Omega_{dk}(\sigma, c) = v_{dk} \exp \left( - \frac{\Delta H_{dk}(\sigma, c)}{k_B T} \right) \left( 1 - c \right) + c \cdot \exp \left( - \frac{E_{\text{int}}(\sigma)}{k_B T} \right) \]

where \( E_{\text{int}}(\sigma) \) is the solute-dislocation interaction energy which also has the same stress dependence as \( \Delta H_{dk} \),
Equation 4.14  \[ E_{\text{int}}(\sigma) = E_{\text{int}}^0 \left[1 - \left(\frac{\sigma}{\tau_{dk}}\right)^0.75\right]^{1.17} \]

where \( E_{\text{int}}^0 \) is the solute-dislocation interaction energy under stress-free condition which is obtained by first-principles calculations.

For the kink-migration, it is believed that the rate-limited step is the time to overcome the largest cluster of solutes along the length of dislocation between superjogs. The superjogs are the sites where the dislocation is pinned to be unable to move. The size of the largest solute cluster appeared in a kink can be determined statistically based on the dislocation density and the kink width. Here, the number of solutes \( m_0 \) in the largest cluster is calculated to be \( m_0 = 23\sqrt{c} \) for BCC W. The detailed derivation can be found in Reference 19. By assuming there is no interaction between the solutes, the migration barrier can be written as [8,19],

Equation 4.15  \[ \Delta H_{\text{km}}(\sigma, c) = m_0 E_{\text{int}} \left[1 - \frac{\sigma - \tau_{\text{thermal}}(c)}{\tau_{\text{km}}(c)}\right]^{3/2} \]

where \( \tau_{\text{km}} \) denotes the kink-migration stress, and \( \tau_{\text{thermal}} \) denotes the athermal component of the stress since the yield stress of the refractory BCC metal becomes roughly temperature-independent above \( \sim 15\% \) of melting temperature. Based on the Peierls-Nabbaro model, the kink-migration stress, \( \tau_{\text{km}} \), is expressed as [8,19],

Equation 4.16  \[ \tau_{\text{km}}(c) = \frac{2}{3} \mu (1 + c\tau') \left\{ \frac{m_0 E_{\text{int}}}{\mu b^3} \right\} 0.94^{-1} \left( \frac{b}{W_k} \right) \]
The athermal stress for pure W is given as $7.5 \times 10^{-5} \mu$ by Brunner [121]. The solute increases the athermal stress, in analogy to the tradition solid-solution hardening effects,

\[
\tau_{\text{athermal}}(c) = \mu (1 + c \tau') \left( 7.5 \times 10^{-5} + \frac{bF_{\text{max}}}{\mu b^3} c \right)
\]

where $F_{\text{max}}$ is the maximum drag force that a solute produces on dislocation, and simplified to be $F_{\text{max}} \approx |E_{\text{int}}|/3 \text{Å}$. As seen from Equation 4.16 and Equation 4.17, same stress scale (Peierls misfit) has also been applied on the stress parameters of kink migration. The final kink migration rate $\Omega_{km}$ is,

\[
\Omega_{km} = \nu_D \exp \left( -\frac{\Delta H_{km}(\sigma, c)}{k_B T} \right)
\]

where the attempt frequency is the Debye frequency.

Finally, it is worth to mention that equations in the solid-solution model discussed above are adapted for a short-range interaction between the solute and dislocation. That is to say, once the dislocation translates by one lattice site, it no longer feels the effect of the solute. However, as shown in the results section later, the solute-dislocation interaction is extended over several lattice sites actually. Therefore, to make the calculated first-principles interaction energy to be automatically compatible with the solid-solution model, the energy value needs to be scaled to represent the change in interaction energy from one lattice site to adjacent one along the (110) plane. For all the solute elements studied in the present work, it is found that a factor of 0.75 is suitable to scale the interaction energy from first-principles. In fact, since this factor reflects the range of chemical interactions near and
around the dislocation core, it needs to be evaluated on case-by-case basis for other system. For example, the factor is found to be 0.5 for the interaction between BCC Mo and 5d transition metal elements [19].

**4.4 Results and discussion**

**4.4.1 Relaxed dislocation core structure**

In the perfect BCC crystal, the orientation of the triangles, which are formed by three adjacent <111> atomic rows, has either clockwise or counter-clockwise chirality. If one triangle has clockwise chirality, its surrounding triangles will all have counter-clockwise chirality. By centering the dislocation in the <111> atomic triangles, two types of dislocation core structures can be obtained, namely, the easy-core and hard-core structures, depending on the sign of the Burgers vector. An easy-core structure reverses the chirality of the triangle from its original chirality to the opposite one, while the hard-core structure makes the three adjacent <111> atomic rows move to the same level. Owing to the large free volume inside the core, the hard-core structure is usually considered to be meta-stable or unstable. In the present work, in order to arrange the dislocation in the <111> triangle which locates in the center of the supercell, Burgers vector of $\frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$ results an easy-core structure and the $\frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$ dislocation has a hard-core structure. Both of the two core structure are built in the supercell initially for relaxation.

The relaxed structures of the two types of dislocation core viewing as a [111] direction projection are shown in Figure 4.3a (easy-core) and 4.3b (hard-core) using both
differential displacement (DD) maps [122] and contours of Nye tensor [94]. The arrows in Figure 4.3 show the displacement along the [111] direction between neighboring atoms measured relative to the perfect BCC crystal. The length of the arrows are normalized; the largest magnitude corresponds to the length of one third of Burgers vector. The full color contours in Figure 4.3 presents the linear-interpolated Nye tensor density, which is calculated following the formulations of Mishin [95]. The components of Nye tensor are the distribution functions of the Burgers vector components of infinitesimal dislocations, which provides informative description of the lattice distortion produced by dislocation. In Figure 4.3, the positive contours present the \([\bar{1}\bar{1}\bar{1}]\) component of Nye tensor, while the [111] component has a negative value. The relaxed easy-core is shown in Figure 4.3a. As seen, the \(\frac{1}{2} [\bar{1}\bar{1}\bar{1}]\) screw dislocation is shown to spread evenly about a central point producing a full D3 symmetry, which agrees with previous simulation results by the dislocation-dipole method [85,87]. The strong dislocated region is localized within 1~2 atomic layers around the dislocation core. It is found that the core structure maintains the eight nearest-neighbor (NN) coordination as in bulk. In the perfect BCC W crystal, the distance between the NNs is about 2.74 Å [104]. However, for the atoms at the dislocation core, it is found that: two atoms at a distance of 2.65Å, two at 2.73Å, and four at 2.80Å, indicating substantial bond distortions at the dislocation core. Dislocation degeneration is not found, indicating the easy-core structure is energetically stable as expected. Figure 4.3b shows the relaxed structure of the hard-core dislocation. A hard-core-to-easy-core transformation has been observed after relaxation. In Figure 4.3b, the original position of the dislocation line before relaxation is marked as a white dot. After relaxation, the
dislocation moves from the original position to the adjacent \(\langle 111\rangle\) triangle, and transforms to an easy-core structure, since the Burger’s vector still keeps to be \(\frac{1}{2}[111]\). This indicates that the hard-core structure of BCC W is energetically unstable, and there is no meta-stable intermediate structure between the hard-core and easy-core structures. Therefore, for the following solute-dislocation calculations, the easy-core structure is always used.

As known, dislocation generates long stress field which is proportional to the inverse of the distance to the dislocation core. In addition, the screw dislocation in BCC W which has extended cores is quite sensitive to the image stress generated at the supercell boundary. Therefore, in order to carefully calculate the interactions between the solutes and an isolated dislocation, effects of the dislocation-dislocation interaction and the supercell boundary on the dislocation core must be eliminated. This requires a large enough region II and III to effectively embed the dislocation in a medium with the harmonic response of the bulk lattice. Figure 4.4 shows the electronic projected density of state (PDOS) of the bulk BCC W and two sites in the relaxed dislocation supercell. The vertical dashed line represents the Fermi level. As seen, the site far away from the dislocation core (in the middle of region II) has a bulk-like bonding environment since its PDOS close to Fermi level is similar to that of the bulk BCC W. In contrast, the PDOS of site at the dislocation core is very different. A larger PDOS value at Fermi level indicates distorted bonding around the dislocation core region, as found by the bond length analysis.
4.4.2 Solute-dislocation interactions

Since the $\frac{1}{2}<111>$ screw dislocation has an extended core structure, the range of the solute-dislocation interaction may not restrict to the lattice sites just besides the dislocation center. Taking Re and Ti as two examples, Figure 4.5a and 4.5b show the calculated first-principles solute-dislocation energy profile for 33 possibly substitutional sites around the screw dislocation core, respectively. In Figure 4.5a and 4.5b, the dislocation is located in the center of the profile, and the calculated interaction energies are scaled by a blue-green-red color bar. Each circle represents a possibly substitutional site, and is colored by the interaction energy of the site. As seen in Figure 4.5a, Re shows attractive interactions with the dislocation. The strongest interaction is found to be at three lattice sites which are closest to the dislocation center. The interaction becomes weaker as Re is placed to farther lattice sites away from the dislocation, in good agreement with the previous calculations [123]. The interaction between Ti and the dislocation is repulsive and much weaker compared to Re (Figure 4.5b). Furthermore, it is interesting to find that, same as the symmetry of the dislocation geometry, the interaction energy profile also has a full D3 symmetry, for both Re and Ti. For the lattice sites have same in-plane ($\{111\}$ plane) distance to the dislocation, they have almost same solute-dislocation energy. This is because the bond bending or distortion at these sites is quite similar, which is determined by the dislocation geometry.

Due to the symmetry of the dislocation geometry, fewer calculations are needed to obtain the interaction energy profiles for the rest of the 19 solute elements (i.e., V, Cr, Mn, Co, Fe, Ni, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, Pt). The solute-dislocation
interaction energy ($E_{int}$) used in the solid-solution model is the maximum energy of the profile. The calculated $E_{int}$ for each solute element are summarized in Table 4.1. In addition, in order to view the trend of solute effects, $E_{int}$ is plotted with respect to the element group number for all the transition metal elements in Figure 4.6. For the solute elements with fewer valence electrons than W, the solute-dislocation interaction energy is found to be small and positive, indicating weak repulsive interactions. On the other hand, for the solutes with more valence electrons than W, their interactions with the screw dislocation are always attractive. In addition, within each group of 3d, 4d, and 5d solute elements, it is found that $E_{int}$ changes from positive to negative values monotonically as the number of valence electrons of the solute elements increases. Similar trend has also been found for the solute-dislocation interaction between Mo and 5d transition metal elements [19]. As discussed in the Section 4.3, solutes could affect the double-kink nucleation by modify the barrier enthalpy locally at the solute sites. Based on Equation 4.13, the solutes with more valence electrons than W can lower the double-kink nucleation barrier at local sites occupied by the solute atom, while the solute in the IV and V group make the dislocation motion even harder in the aspect of double-kink nucleation.

Furthermore, based on the relaxed solute-doped dislocation core structure, we would be able to calculate the Peierls misfit, which reflects a global change of the stress scale of kink nucleation and migration. The calculated Peierls misfits of all the solute elements are listed in Table 4.1 as well, and the $\delta E$ vs. displacement fitting results are shown in Figure 4.7. It is found that the Peierls misfits are also positive for the solutes which have positive interaction energies, which means these solutes increases not only the nucleation barrier locally but also the stress scale of dislocation motion as well. Meanwhile,
the solutes of VI, VII and VIII group could increase nucleation of double kinks and provide more favorable nucleation sites due to the negative Peierls misfits and interaction energies. In addition, one may notice that the Peierls misfits for the IX and X solutes are not calculated. This is due to the change of core geometry caused by a strong attractive interaction between solutes and dislocation, which will be discussed in details later.

4.4.3 Predictions of critical resolved shear stress

Based on Equation 4.3, Equation 4.13, and Equation 4.18, the critical resolved shear stress could be solved as a function of solute concentration and temperature at a constant strain rate by inputting the calculated interaction energy and Peierls misfit. The predicted CRSS of W-Re at 298K is plotted as function of Re concentration in Figure 4.8. As seen, the attractive interaction and negative Peierls misfit of Re leads to a strength softening at low concentration, which is due to a promotion of double-kink nucleation. With additional solutes, the solute-induced pining effects on the kink migration become more dominate, resulting in a hardening effect on CRSS. A crossover point can be found between the softening and hardening effect. In addition, it has been found the crossover happens at lower concentration for higher temperature, since the double-kink nucleation is easier than kink migration at high temperatures. Available experimental data is also included in Figure 4.8 for comparison [9,15]. A good agreement between the prediction and the experiments are found for the solute concentrations less than 10 at.%s. The discrepancy at higher concentration may be due to the solute-solute coupling effects on the double kink nucleation which could not be captured by current solid-solution model.
The effects of other solutes on the CRSS of BCC W at 298K are shown in Figure 4.9 as a function of solute concentration. It is found that the solute elements in IV and V groups provide slight hardening effects on BCC W. This is because the repulsive interactions between these solute elements and dislocation increase the double-kink nucleation barrier at the solute site. The strongest effect is from Hf which has the largest repulsive interaction energy relative to other IV and V solute elements. For the solutes with negative interaction energy and Peierls misfit, a softening effect can be found at low concentration range as expected. Fe, Ru and Os produce a strong softening effect initially for the solute concentration less than 1 at.% This is due to their large attractive interactions which results a substantial change in the double-kink nucleation barrier. However, their large interaction energies also quickly lead to the hardening effects at higher concentrations since the solute pinning effects on kink migration easily become dominate. Furthermore, it is found that alloying W with Mn, Al and Tc leads to a moderate softening on CRSS, similar to the effects of Re. Mo and Cr seem to produce a weak softening effect on CRSS continuously over the tested concentration range. However, it should be aware that these two solute elements may not soften BCC W further at higher concentrations by following the trend of the predictions since the solid-solution model used in here is more reliable in low alloying concentration range. The predicted softening-hardening crossover concentrations for the solutes for are summarized in Table 4.2. The predictions for Tc, Ru, Re and Os are in a good agreement with available experimental data [3]. Among the examined solute elements which have softening effects, Al and Mn seem to be the most promising alternatives to Re potentially, since Ru and Os are also precious metals and Fe
has bare solubility in BCC W [124]. The optimizing alloying concentrations for Al and Mn to obtain the largest softening effect are about 2.9 at.% and 2.5 at.%, respectively.

### 4.4.4 Solute effects on dislocation core geometry

As mentioned above, it is found that the solute elements in the IX and X groups lead to significant local reconstruction of the dislocation geometry in BCC W. Taking Ir as an example, Figure 4.10 shows the relaxed core geometries without Ir and with Ir substitutions at five different core sites, respectively. The five core sites substituted by Ir atoms are marked as blue dots and numbers; the positions of dislocation center before relaxation are marked by dashed circles. Compared to the dislocation structure of pure BCC W (Figure 4.10a), significant changes in core geometry can be found when the Ir atoms are placed at the lattice sites with the first-, second- and third-nearest distance to the initial dislocation position, as shown in Figure 4.10b, 4.10c and 4.10d, respectively. Furthermore, it is found that the changes in the core geometry induced by Ir atom also result in a movement of dislocation center after relaxation, as shown by the contour plots of Nye tensor in these three figures. When the Ir atom is placed at site 1 (Figure 4.10b), the dislocation moves from its initial position towards the adjacent <111> triangles. Correspondingly, the core structure is changed from the easy-core geometry to a degenerate structure which is more close to have a hard-core geometry. As the Ir atom is placed a little bit farther away from the dislocation center, such as at sites 2 and 3, the dislocation is found to split alone the {110} planes, resulting in movements of the dislocation core towards to the Ir atom sites (Figure 4.10c and 4.10d). Therefore, the Peierls misfits cannot be able to
be calculated by displacing the \( <111> \) atomic column since the dislocation moves already after the structure relaxation. When the Ir atom is placed at the positions (sites 4 and 5) far away from the dislocation core, the solute effects on the core geometry become neglectable (Figure 4.10e and 4.10f). Similar solute effects on the dislocation geometry have been also observed for Fe, Ni, Rh, Pd and Pt.

Accompanied by a significant core geometry distortion, the calculated solute-dislocation interaction energy of Ir is also very negative, about -1.08 eV. It should be noted that the barrier enthalpy of kink nucleation of pure W is only 1.107 eV. Based on Equation 4.13, the nucleation barrier can be extremely lowered at the solute sites, which means the double-kind nucleation could happen easily at low temperatures even without external stress. As shown by the present calculations, the system energy is minimized by moving the dislocation towards to the Ir sites. In fact, due to this strong attractive interaction, an initially straight screw dislocation in a field of randomly distributed Ir atoms is expected to bow out into regions of the solid containing solute sites by lowering its energy. Meanwhile, the dislocation is also pinned by the solute sites, which results a solute hardening effect [125]. Therefore, it is proposed that alloying W with the solute elements in the IX and X groups will increase the CRSS of W rather than soften it, even though these solutes elements could lower the double-kind nucleation barrier locally.

In fact, besides the solute elements in the IX and X groups, rest solute elements are found to distort the dislocation core geometry to some extent. It is found that the larger magnitude of the solute-dislocation interaction correlates to a stronger distortion of core structure. Figure 4.11 shows the relaxed core structures of W-Hf, W-Re, W-Os and W-Pt, respectively. The solute substitutional sites are marked as blue dots. As seen from Figure
4.11a and 4.11b, the effects of Ta and Re on dislocation geometry are neglectable (Nye tensor contours are very close to pure W (Figure 4.3a)). Correspondingly, as shown in Table 4.1, the solute-dislocation interaction energies of Ta and Re are also relatively small compared to that of Os and Pt. On the other hand, Os is found to induce obvious distortion on core geometry, as shown in Figure 4.11c. The dislocation seems to move from its initial position which is located in the center of the <111> triangle towards to the left side, as indicated by the contours of Nye tensor. As the interaction between the solute and dislocation becomes even stronger that of W-Os, for example W-Ir and W-Pt, the dislocation core moves to the adjacent lattice triangles, as shown by Figure 4.10b and Figure 4.11d. Further scrutinizing the atomic bonding environment at the dislocation core, it is found that the observed reconstructions of core geometry actually result from a solute-induced atomic bond distortion. For pure W, as mentioned previously, the atoms at the dislocation core sites still hold 8-nearest-neighbor coordination as the perfect BCC crystal. As shown by the insets in Figure 4.11a and 4.11b, the number of nearest-neighbors of the Ta and Re atoms are same as pure W. However, the number of nearest-neighbors of Os is found to be 9 by using the same distance cutoff. As shown by the inset in Figure 4.11c, compared to the 8-nearest-neighbor coordination in W-Ta and W-Re, one more W atom has been attracted to move close to the Os atom. For Pt, two more W atoms become its nearest-neighbors, as shown by the inset in Figure 4.11d. As a result, the dislocation core geometries of W-Os and W-Pt are significantly distorted.
4.5 Conclusion

As an effort for searching Re alternative elements to soften BCC W, improving ductility at low temperatures, the solute-induced solid-solution softening and hardening has been systematically studied in BCC W for twenty-one alloying elements. The core structure of the single the ½<111> screw dislocation and its interaction with solute atoms are directly computed via DFT based first-principles calculations with the flexible boundary condition method. As combined, the calculation results with an improved solid-solution softening model of plasticity, we were able to quantitatively predict the CRSS of BCC W with changing solute concentration at room temperature. It was found that:

1. In BCC W, the stable configuration of the ½<111> screw dislocation is the easy-core geometry. The hard-core geometry is found to be energetically unstable and degenerate to the easy-core geometry after relaxation.

2. The solute elements in the IV and V group have weakly repulsive interactions with the ½<111> screw dislocation, while other solute elements (including Al) show attractive interactions with the dislocation as reflected by the negative interaction energies. For the transition metal elements, the solute-dislocation interaction increases dramatically as the number of valence electrons of the solute elements increases. The Peierls misfits is calculated to be positive for the solutes which have positive interaction energies, and vice versa.

3. The enthalpy barrier and stress scales for dislocation motion are strongly influenced by the solute atoms at the dislocation core. The solute affects the double-kink nucleation by modifying the enthalpy barrier locally and changing the stress scale
of the nucleation barrier globally. On the other hand, the kink migration is limited by the solute pining effects from largest solute cluster along the dislocation line.

(4) Due to the negative solute-dislocation interaction energy and Peierls misfits, small additions of the solute elements in the VI, VII and VIII group and Al could soften the BCC W by promoting the nucleation of double kinks. Hardening effects are observed with increasing the solute concentration, which is caused by the solute pinning effect on kink migration. The softening-hardening crossover concentrations are predicted, and compared remarkably well with available experiments in the literature.

(5) Accompanied by a strong attractive interaction, the solute elements in the IX and X groups are found to distort the dislocation core geometry significantly, resulting in a motion of the dislocation towards to the solute site after structure relaxation. Due this solute-induced structure distortion, it is believed that these solutes will mainly result in a solute pinning effect on the dislocation motion in BCC W, even at very low solute concentrations.

Among the examined solute elements which have the softening effects, Al and Mn seem to be the most promising alternatives to Re to improve the ductility of BCC W at low temperatures. The present work provides the fundamental understanding of the solute effects on the plastic strength of BCC W for future rational design of novel W alloys.
Table 4.1 Calculated solute-dislocation interaction energy ($E_{int}$) and Peierls misfit. Calculations of the Peierls misfit for solute elements in Group IX and X are not performed due to the change of dislocation core geometry induced by these solutes. The solute elements have softening effects at low alloying concentrations are marked by green. The solute elements with continuous hardening effects are marked by red.

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<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Interaction energy $E_{int}$ (eV)</th>
<th>Peierls misfit</th>
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<td>0.077</td>
<td>0.065</td>
<td>0.000</td>
<td>-0.238</td>
<td>-0.628</td>
<td>-1.086</td>
<td>-1.223</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.437</td>
<td>0.354</td>
<td>0.000</td>
<td>-0.440</td>
<td>-0.606</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.2 Predicted soften-hardening crossover concentrations for the solute elements at 298K. Available experimental data are included for comparison.

<table>
<thead>
<tr>
<th>X</th>
<th>Predict</th>
<th>Expt.[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.9 at.%</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>2.5 at.%</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.8 at.%</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>4.0 at.%</td>
<td>2.5 at.%</td>
</tr>
<tr>
<td>Ru</td>
<td>0.7 at.%</td>
<td>0.55 at.%</td>
</tr>
<tr>
<td>Re</td>
<td>7.5 at.%</td>
<td>6.5 at.%</td>
</tr>
<tr>
<td>Os</td>
<td>1.1 at.%</td>
<td>0.8 at.%</td>
</tr>
</tbody>
</table>
Figure 4.1 Supercell structure for first-principles simulations with flexible boundary condition method. One isolated dislocation is placed in center of the supercell. The supercell is separated into regions I (yellow), II (blue) and III (grey).
Figure 4.2 Schematic illustration of the dislocation motion under the double-kink nucleation and kink migration mechanism in BCC W. (a) Double-kink nucleation; (b) Kink migration.
**Figure 4.3** Relaxed dislocation core geometry viewed by Nye tensor and DD plot. (a) Easy-core structure; (b) hard-core structure. The position of the dislocation core before relaxation is marked as white circles.
Figure 4.4 Projected density of state (PDOS) of electrons for the atomic sites in the $1/2\langle111\rangle$ dislocation and bulk BCC W. The Femi energy is labeled by a vertical dash line.
Figure 4.5 Solute-dislocation interaction energy profile for (a) Re and (b) Ti. Each circle is a possibly substitutional lattice site for the solute atom in an atomic row, and colored by the value of the interaction energy at the site based on the color bar. The dislocation is located in the center of the profile.
Figure 4.6 Solute-dislocation interaction energy ($E_{int}$) of transition metal elements as a function of element group number.
Figure 4.7 $\delta E$ vs. atomic column displacement fitting.
Figure 4.8 Predicted CRSS for W-Re alloy as a function of Re concentration at 298K. Two sets of experimental data are included for comparison [9,15].
Figure 4.9 Predicted CRSS for W-X alloy as a function of solute concentration at 298K.
Figure 4.10 Relaxed dislocation core structures for pure W and W-Ir alloys. (a) Pure W. (b)-(f) Ir atom at different atomic sites; from the sites near dislocation core to the sites far away. The sites occupied by Ir atoms are labeled by blue circles.
Figure 4.11 Relaxed dislocation core structures of (a) W-Ta (b) W-Re (c) W-Os (d) W-Pt.

The inset in each sub-figure shows the first-nearest neighbor W atoms of the solute atoms.
Chapter 5

Segregations of Cr, Ni, Cu, Zr, Ta and W on BCC-Fe Grain Boundaries

5.1 Introduction

Frist-principles approaches based on density functional theory (DFT) have been proven to be efficient and reliable in investigating the solute segregation behaviors of the Fe GBs [126–136]. The focus of the most previous works is on the segregation of light elements, such as H, B, C, N, O, S and P [126,133,134,137–139], while a few works have looked into the segregation behaviors of several individual transition metal elements [128,131,140]. Great efforts have been made in these works to investigate the solute segregation behaviors in terms of site preference [131], atomic structure [136], magnetism [130,136], and GB cohesion [126–129,132–135,137,139,140]. However, to the author’s knowledge, the origin of the solute segregation energy is rarely investigated in a quantitative manner with respect to the strain and chemical contributions, which could provide valuable guidance for the estimations of the solute segregation enthalpy in the analytical thermodynamic models mentioned above.
In this part of the dissertation, segregation of six transition metal elements (Cr, Ni, Cu, Zr, Ta and W) on the Σ3 (111)[110] tilt boundary in BCC Fe are investigated systematically via first-principles calculations in terms of the solute effects on the GB energy, GB area and solute segregation energy. It is found that the reduction in the GB energy is mainly due to the solute segregation process instead of an extension of the unit GB area. The quantification of the solute segregation energy is discussed in terms of the crystalline lattice distortion and the difference between the chemical bond energies in and out of the GB region.

It has also been observed that the solute segregation at Fe GB could lead to GB embrittlement [127,129] or strengthening [128], dictated by GB cohesive strength based on the intergranular fracture mechanism [141]. Here, first-principles tensile tests are performed to mimic the response of the clean and solute segregated GBs to a uniaxial tensile strain normal to the GB plane. The dynamic change in atomic and electronic structures are investigated to provide physical insight into the effects of solute segregation on the failure mechanisms of the Σ3 (111)[110] tilt boundary in BCC Fe.

5.2 Computational details

The Σ3 (111)[110] grain boundary is created based on coincidence site lattice (CSL) theory [142]. The calculated equilibrium lattice parameter for bulk BCC Fe, $a=2.82$ Å, in a good agreement with experimental measurements [143], is used for constructing the supercell. The supercell consists of twelve (111) atomic layers and its image mirrored with respect to the (111) plane, as shown in Figure 5.1a. The supercell coordinates are
related to the BCC lattice index in terms of $2[1\overline{1}0]_{BCC} \times 4[111]_{BCC} \times [11 \overline{2}]_{BCC}$. Two GBs are included in one supercell due to the periodic boundary conditions and apart from each other for over 10 Å to avoid the interactions between each other. To investigate the effects of segregation of Cr, Ni, Cu, Zr, Ta and W, one Fe atom is substituted by a solute atom (marked as red, shown in Figure 5.1a) at each GB plane, giving an in-plane concentration of 25 at.%. A reference BCC supercell with the same amount of atoms and initial size, but without GB, is constructed as shown in Figure 5.1b, with an alloying content of 2.08 at.%. The GB energy, $\gamma$, is defined as,

**Equation 5.1**

$$\gamma = \frac{E_{GB} - E_{Bulk}}{2A}$$

where $E_{GB}$ and $E_{Bulk}$ are the total energies of the supercells with and without GB, respectively, and $A$ denotes the grain boundary area per supercell. The factor 2 accounts for the presence of two GB planes per supercell.

First-principles calculations based on density functional theory (DFT) are performed to relax the supercells and obtain their total energies. The projector augmented wave method (PAW) [99] and the exchange-correlation functional depicted by the generalized gradient approximation (GGA-PW91) [75], as implemented in the Vienna Ab-initio Simulation Package (VASP) [57], are employed. The energy cutoff of the plane wave is set as 350 eV. The reciprocal-space energy integration is performed by the Methfessel–Paxton method [100] for structural relaxations. Based on the supercell geometry, a Γ-centered $5\times 2\times 6$ grid is applied for sampling the wave functions. The energy convergence criterion of the electronic self-consistency is set to be $10^{-6}$ eV/atom. Collinear spin alignment was applied in the present calculations due to the ferromagnetic nature of BCC
Fe at low temperatures. Furthermore, in the case of Cr segregation, two magnetic configurations are considered because of the anti-ferromagnetic feature of Cr with its initial spin direction either to be same as or opposite to the one of Fe atoms. The four-parameter Birch-Murnaghan equation of state is used to determine the equilibrium state of the supercells [61]. After relaxation, the final total energy calculations are performed by using a tetrahedron method with Blöchl corrections [101]. The contour plots of the differential charge density are generated using VESTA [102,103].

The ideal cohesive strength of the segregated GBs is investigated by first-principles tensile tests [144]. A uniaxial engineering strain of 2.5% are incrementally applied to the relaxed supercell along the [111] bcc direction ([010] direction of the supercell), which is normal to the GB plane. At each strain step, the supercell is constrained along the strained direction but allowed to relax in other directions. Meanwhile, all atomic positions are allowed to relax until the Hellman-Feynman forces become smaller than 20 meV/Å⁻¹. After relaxation, all the stress components of the supercell are almost zero, except $\sigma_{22}$, which is the true stress responses to the applied strain. The applied strain is continuously increased until the crystal structure losing its mechanical stability. The ultimate ideal tensile strength is defined to be the cohesive strength of the GB in the present work.
5.3 Results and discussion

5.3.1 Effects of solute segregations on GB energy

The total energies of the supercells with GB (E_{GB}) and without GB (E_{Bulk}), and the GB area per supercell (A_{GB}) for each system are summarized in Table 5.1 along with the GB energies (\gamma_{GB}) without or with the effects of solute segregations calculated from Equation 5.1. Here, we report that the interfacial energy per area of the \Sigma 3 (111)[1\bar{1}0] GB in pure BCC Fe is about 1.562 J/m^2, in a good agreement with previous theoretical studies [136,145,146]. As shown in Table 5.1, the largest reduction in the GB energy is by the segregation of Zr. In addition, the GB energy is also reduced effectively by Ta and moderately by Cu and W. The reductions due to the segregations of Ni and Cr are not significant. In general, since the GB energy is the driving force for grain growth, a reduction in GB energy is considered to reinforce the heat-resistance of grain growth in the nanocrystalline alloys. Therefore, based on the present calculations, Zr and Ta are expected to stabilize the gain size of BCC Fe further in against temperatures compared to other alloying elements. This has been confirmed by the previous experimental studies. It was found that the highest temperature at which an Fe-based alloy keeps grain sizes less than 100 nm, being considered as a measure of stability, relates as follows: T_{Fe-1at.%Zr} > T_{Fe-1at.%Ta} > T_{Fe-1at.%Ni} \approx T_{Fe-10at.%Cr} \approx T_{pure-Fe} [22]. Furthermore, the regularity of the segregation effects of Zr, Ta, Ni and Cr observed in the present work is also in a good agreement with the predictions from a previous phenomenological thermodynamic model [34].
It is interesting to further discuss the origin of the reduction in the GB energy induced by the segregating solutes. In the analytical thermodynamic models mentioned in Chapter 1, the reduction in GB energy is considered to be determined by the segregation free energy, which is calculated by a general equation [35],

**Equation 5.2** \( \Delta \gamma = \Gamma_x \Delta G_{seg} \)

where \( \Delta \gamma \) denotes the change of the GB energy caused by solute segregation, and \( \Delta G_{seg} \) denotes the segregation free energy, which is the first derivate of Gibbs energy of the system with respect to the change of the solutes from grain interior to GB with fixed temperature, pressure and GB area [35],

**Equation 5.3** \( \Delta G_{seg} = \left( \frac{\partial G}{\partial n_x} \right)_{A,T,P} \)

Another term in Equation 5.2, \( \Gamma_x \), is so-called the grain boundary excess amount of solute, which can be calculated as [37],

**Equation 5.4** \( \Gamma_x = \frac{2(x_{gi}^{x} - x_{GB}^{x})}{A} \)

where \( x_{gi}^{x} \) and \( x_{GB}^{x} \) are the mole-fraction of the solutes in grain interior and at GB, respectively, and \( A \) is the unit GB area. In these analytical thermodynamic models, an assumption has been made that \( A \) is always a constant which means there is no change of the unit GB area when the solute atoms substitute solvent atoms at GB [37]. Based on this assumption, for a given and fixed distribution of the solute atoms in grain interior and at GB, the reduction in GB energy is fully determined by the segregation energy, \( \Delta G_{seg} \), However, to the best knowledge of the present authors, such assumption has not been validated yet.
Here we could define a closed system containing two supercells. At the initial state, one supercell is only composed by Fe atoms and contains two cleaned Σ3 GBs, as the structure shown in Figure 5.1a; another supercell is constructed as BCC bulk lattice in which two Fe atoms are substituted by two solute atoms, as shown in Figure 5.1b. After a process of segregation, the solute atoms move from bulk matrix to the clean GB forming the segregated GBs and pure BCC Fe bulk. Based on Equation 5.1, the change of GB energy caused by the segregation can be expressed as,

**Equation 5.5**

\[
\Delta \gamma = \gamma_{GB}(Fe, X_{seg}) - \gamma_{GB}(Fe) = \frac{E_{GB}(Fe, X_{seg}) - E_{Bulk}(Fe, X_{sol}) - E_{GB}(Fe) - E_{Bulk}(Fe)}{2A_x}
\]

where \( \gamma_{GB}(Fe, X_{seg}), \gamma_{GB}(Fe), A_x \) and \( A_0 \) are the GB energy and GB area per supercell of the segregated GB and the clean GB, respectively. \( E_{GB}(Fe) \) and \( E_{Bulk}(Fe) \) are the total energies of the pure Fe supercells constructed with and without GBs, respectively, whereas \( E_{GB}(Fe, X_{seg}) \) and \( E_{Bulk}(Fe, X_{sol}) \) are the total energies of the supercell containing solute-segregated GBs and its corresponding bulk reference, respectively. Based on Equation 5.5, the reduction in the GB energy can either be attributed to an extension of the GB area (\( A_x > A_0 \)) or the relative energy changes caused by the solute segregation. For further investigation, the relative changes of the GB energy, \( \eta_x \), and the GB area, \( \lambda_x \), with respect to the unalloyed GB, are calculated for each alloyed GB, where \( \eta_x = \frac{\Delta \gamma}{\gamma_0} \) and \( \lambda_x = \frac{A_x - A_0}{A_0} \). As shown in Figure 5.2, the relative changes of the GB area after solutes segregation are all very small. The largest extension of GB area is only 1.2% due to the
segregation of Zr. This indicates that segregating solute atoms does not strongly affect the unit GB area, even the solute has a large atomic size (i.e., Zr and Ta). Therefore, the approximation of $\Gamma$ in the previous analytical thermodynamic models [37] is reasonable and validated by the present quantum mechanical model. On the other hand, it is noted that $\eta_x$ is much larger than $\lambda_x$ as shown in Figure 5.2, which means the reduction in GB energy caused by the solute segregation cannot be attributed to the GB area extension. By the approximation of $A_x \approx A_0$, Equation 5.5 can be re-written as,

**Equation 5.6**

$$\Delta \gamma = \frac{\left[ (E_{\text{bulk}}(Fe) - E_{\text{GB}}(Fe, X_{\text{seg}})) - (E_{\text{GB}}(Fe) + E_{\text{bulk}}(Fe, X_{\text{sol}})) \right]}{2A_0}$$

In fact, the segregation energy of one solute atom ($\Delta E_{\text{seg}}$) is usually defined as [131],

**Equation 5.7**

$$\Delta E_{\text{seg}} = \frac{1}{2} \left[ (E_{\text{bulk}}(Fe) - E_{\text{GB}}(Fe, X_{\text{seg}})) - (E_{\text{GB}}(Fe) + E_{\text{bulk}}(Fe, X_{\text{sol}})) \right]$$

At 0K, since there is no contribution of entropy to the free energy, we have $\Delta E_{\text{seg}} = \Delta G_{\text{seg}}$.

Therefore, Equation 5.6 could be written as,

**Equation 5.8**

$$\Delta \gamma = \frac{\Delta E_{\text{seg}}}{A_0} = \frac{\Delta G_{\text{seg}}}{A_0}$$

Since $A_0$ is a constant, the present atomic model indicates that the reduction in GB energy provided by the segregating solutes is indeed determined by the segregation energy, $\Delta G_{\text{seg}}$, as assumed in the previous analytical thermodynamic models [27,28,31,35–37,39,40].
5.3.2 Energy decomposition of the solute segregation energy ($\Delta E_{\text{seg}}$)

In order to further understand the interaction mechanisms between the solutes and GBs in the aspects of strain and chemical contributions, the total solute segregation energy, $\Delta E_{\text{seg}}$, can be decomposed into two parts,

**Equation 5.9**

$$\Delta E_{\text{seg}} = \Delta E_{\text{seg}}^{\text{str}} + \Delta E_{\text{seg}}^{\text{chem}}$$

where $\Delta E_{\text{seg}}^{\text{str}}$ refers to the contribution from the strain releasing and $\Delta E_{\text{seg}}^{\text{chem}}$ refers to the contribution from the change of chemical bonding. Here, the strain contribution, $\Delta E_{\text{seg}}^{\text{str}}$, is defined as,

**Equation 5.10**

$$\Delta E_{\text{seg}}^{\text{str}} = \frac{1}{2} \left[ (E^{\text{str}}_{\text{bulk}}(Fe) + E^{\text{str}}_{\text{GB}}(Fe, X_{\text{seg}})) - (E^{\text{str}}_{\text{GB}}(Fe) + E^{\text{str}}_{\text{Bulk}}(Fe, X_{\text{sol}})) \right]$$

where $E^{\text{str}}_{\text{GB}}(Fe)$ and $E^{\text{str}}_{\text{Bulk}}(Fe)$ are same as the ones in Equation 5.5, and $E^{\text{str}}_{\text{GB}}(Fe, X_{\text{seg}})$ and $E^{\text{str}}_{\text{Bulk}}(Fe, X_{\text{sol}})$ are defined and calculated as follow: once the two supercells (i.e., with and without GBs) with solute atoms have been fully relaxed, the solute atoms are removed from the relaxed supercells. Then the total energies of the operated supercells are calculated statically, i.e., $E^{\text{str}}_{\text{GB}}(Fe, X_{\text{seg}})$ and $E^{\text{str}}_{\text{Bulk}}(Fe, X_{\text{sol}})$. Therefore, $\Delta E_{\text{seg}}^{\text{str}}$ actually represents the energy reduction in the system by reducing the distortion strain in the host BCC Fe lattice when the solute atoms combined with clean GB forming the segregated GB. Similar analysis of the strain energy reduction has been seen in the previous studies about the solute-defect bindings [147,148]. The chemical contribution, $\Delta E_{\text{seg}}^{\text{chem}}$, can be obtained based on Equation 5.8. The calculated $\Delta E_{\text{seg}}$, $\Delta E_{\text{seg}}^{\text{str}}$ and $\Delta E_{\text{seg}}^{\text{chem}}$ of each alloy system are
listed in Table 5.2 for comparison. As seen, for all the solute elements, both of \( \Delta E_{\text{seg}}^{\text{str}} \) and \( \Delta E_{\text{seg}}^{\text{chem}} \) have notable contributions to the total segregation energies, which indicates that the total solute segregation energy cannot be attributed to either the strain contribution or chemical contribution only, but a combination of both the contributions. Even for the solutes with large size misfit, such as Zr and Ta, the energy reduction due to the change of chemical bonds is also considerable. In addition, since the atomic coordination numbers of solute atoms in the matrix lattice and at GBs are same for the \( \Sigma 3 \) GB, the non-zero values of the chemical contributions indicate that the chemical bond interactions at GB are very different from that of grain interior.

For the purpose to guide the selection of alloying elements, it is interesting to further investigate how these energy quantities are related back to some “easy-to-get” quantities of the solute elements, such as atomic size. Usually, the release of the elastic strain energy is considered to be associated with the size misfit between solute and solvent atoms. In Figure 5.3, \( \Delta E_{\text{seg}}^{\text{str}} \) of each type of the solute is plotted as a function of atomic size misfit, which is defined as the absolute difference between the atomic volumes of BCC Fe and the solute elements with BCC crystal structure [61]. As seen, the magnitude of \( \Delta E_{\text{seg}}^{\text{str}} \) increases with the atomic size misfit. Evidently, a larger atomic size misfit leads to a stronger lattice distortion, and results in a large strain energy penalty in the bulk phase. By segregation, the strain energy penalty induced by large solute atoms can be reduced, since the atomic packing density at GB is relatively low. As a result, the solute atom with larger size will exhibit a more negative segregation energy and stronger segregation tendency. Similar findings have been also reported in the previous study of the BCC Fe \( \Sigma 5 \) GB [131].
Furthermore, it is noted that there is a correlation between $\Delta E_{\text{seg}}$ and $\Delta E_{\text{str}}$. As seen in Figure 5.4, $\Delta E_{\text{seg}}$ becomes more negative monotonically as the magnitude of $\Delta E_{\text{str}}$ increased, despite of the discrepancy of the Fe-Cu system. It is worth to indicate that such trend does not imply the chemical contributions of the solute elements are all same. It is found that, as a certain amount of strain energy is reduced, the system also benefits of a comparable energy reduction due to the changes of the electronic bonding between solute and Fe atoms after segregation. Based on the trend, it seems the atomic size misfit could be a simple criterion for selecting solute elements which have strong segregation tendency at the GB and thus reduce the GB energy. The off trend deviation of Cu is because the magnitude of $\Delta E_{\text{seg}}^{\text{chem}}$ is much larger than that of $\Delta E_{\text{seg}}^{\text{str}}$. This is possibly due to a strong electronic repulsiveness between the Fe and Cu atoms in the bulk lattice, which could be reflected by the very positive mixing enthalpy of the BCC Fe-Cu solid solution, even in dilute composition range [149].

5.3.3 Effects of solute segregations on GB cohesion

5.3.3.1 First-principles tensile test

In order to investigate the effects of alloy segregations on the mechanical strength of the GBs, the first-principles tensile tests are employed to mimic the response of GBs to a uniaxial tensile strain normal to the GB plane. These calculations characterize the ideal strength which comprises an upper bound on the cohesive strength of the GBs. Figure 5.5
shows the stress-strain relations for the clean GB and the GBs with solutes. As seen, for each strain-stress curve, the stress increases monotonically with the loading strain until the strain reaches a critical value. As the strain is above the critical value, the stress starts to drop, indicating that the GB structure has lost its mechanical stability. Therefore, the ideal tensile stress at the critical strain is defined as the GB cohesive strength, which is considered to be a measure of resistance to crack initiation at GB region.

The cohesive strengths and the critical strains of the clean GB and the solute-segregated GBs are summarized in Table 5.3. For the clean GB, the cohesive strength is about 22.9 GPa at a critical strain of 25%, in a good agreement with previous theoretical studies [27,29]. The maximum ideal tensile stress of the bulk BCC Fe in the [111] direction is reported to be 27.5 GPa [58], larger than the GB cohesive strength, implying the GB is indeed the weakest link. For the segregated GBs, the effects of different solute elements on the GB cohesive strengths are various. As shown in Table 5.3, on the one hand, reductions in the GB cohesive strengths are found due to the segregations of Zr, Cu and Ni, indicating these elements could lead to embrittling of Fe GBs in practice. In fact, Cu is known as intergranular impurity to have harmful effects on the GB cohesion in BCC Fe, as shown in the previous experimental measurements and first-principles calculations [29,59]. In addition to Cu, Zr is found to have the largest GB embrittling potency. Therefore, alloying large amount of Zr in the nanocrystalline Fe alloys may affect the mechanical strength of the materials detrimentally, although it could reduce the GB energy to stabilize the grain size in the meanwhile. On the other hand, it is found that the Fe Σ3 GB could be strengthened by segregations of Cr, Ta and W, which are usually used as the strengthening components in the alloying metallurgy. The strengthening potency follows the order: W >
Ta > Cr. By considering the effects of solute segregation on both GB energy and cohesion, among the six solute elements studied in the present work, Ta seems to be the best alloying addition for nanocrystalline Fe alloys as it could stabilize the grain size and reinforce the GB cohesive strengthen at the same time.

5.3.3.2 GB fracture path and solute effects

To determine the fracture path and plane of the GBs, the variations in the atomic bonds length as a function of strains are investigated. As shown in Figure 5.6a, the constructed GB structure is composed by four (110)-atomic layers in an ‘ABAB…’ stacking sequence. For sake of representing conveniently, these four atomic layers are labeled as I, II, III and IV, as shown in the Figure 5.6a. For the structure with unalloyed GB, the four atomic layers are equivalent due to the symmetry of the BCC crystal structure. The view along the [110] direction of the layer I is shown in Figure 5.6b. When the strain applied along the [111] direction, the layer I will be stretched horizontally and simultaneously shrink along the [112] direction. Five atomic bonds are chosen to investigate their response to the loading strains (labeled as dashed arrows in Figure 5.6b). Among them, $d_2$ and $d_3$ are the bonds between the atom in the GB plane and its first-nearest neighbors in the (110) plane, while $d_1$ is the bond between the GB atom and its second-nearest neighbor. $d_4$ is the bond between the atom just beside the GB plane and its first-nearest neighbor in the grain interior. $d_5$ is the bond between a pair of first-nearest neighbors in the grain interior. It is noted the $d_1$, $d_4$ and $d_5$ are the same type atomic bonds which are all along the loading direction. Figure 5.6c shows the relative changes of the
lengths of these five atomic bonds with respect to the overall strain applied on the supercell. After the overall strain increased from 0 to 0.25 (critical strain), the elongation of bond length is 31.6% for d_2, 27.5% for d_4, and only 18.0% for d_5. Apparently, the d_2 bond is the weakest link to initiate fracture during the tensile deformation. In addition, at the strain of 0.25, the d_1 bond is elongated about 13.0%, larger than the net value of the overall strain along its bond direction, indicating the d_1 bond is easy to break as well. Besides, the length of d_3 bond is almost invariant with respect to the loading strain. Therefore, it can be concluded that the fracture may first be generated due to the broken of d_1 and d_2 bonds, and then spread to break the d_4 bond. By taking the stacking sequence of the (110) layers into account, the de-cohesion plane of the tested GB structure is determined to be the (111) plane, which is the GB plane.

It is interesting to note that there exists a stress plateau in the tensile curve of the unalloyed GB after the applied strain passes the critical value (Figure 5.5), which is also reported by the previous study [129]. Meanwhile, for the solute segregated GBs, the stress drops rapidly above the critical strains, where the stress plateau is not seen (Figure 5.5). This indicates that, the GB fracture with solute segregation may suddenly happen after the system loses mechanical stability, in a different way compared to the clean GB. For each solute-segregated GB, the bond lengths of all the four (110) layers are analyzed in a same way as the clean GB. It needs to point that only layer I contains the solute atoms since the in-plane segregation concentration is 25 at.%. It is found that the response of the d_1 bonds of the solute-segregated GB to the applied strain is very different from that of the unalloyed GB. Taking Ta-segregated GB as an example, Figure 5.7a shows non-uniform elongations of the d_1 bonds of the four (110) layers as a function of the loading strain. Since the layer
II and IV are identical, the bond analysis of these two layers is presented by one dataset. As seen, the $d_1$ bond in the layer I is stretched less than the rest three as the strain increased close to the critical value, indicating the Fe-Ta $d_1$ bond is relatively stronger than the Fe-Fe $d_1$ bonds in other three layers. When the loading strain is above the critical value (0.225), sudden and tremendous increases on the length of the $d_1$ bonds are observed in the layer II, III and IV, indicating the occurrence of bond breaking. It is believed that the rapid drop of the stress results from this inhomogeneous bond breaking, which is not seen in the case of the unalloyed GB. In addition, the bond breakings of the Zr-segregated GB is found to share the same trends with the Ta-segregated GB as shown in Figure 5.7b. On the other hand, the bond breaking could be seen in the layer I, when the solute atom is Cu, Cr, W or Ni. Taking Cu as an example, as shown in Figure 5.7c, the Cu-Fe $d_1$ bond in the layer I is weaker than the Fe-Fe $d_1$ bond in the layer III. In addition, the Fe-Fe $d_1$ bonds in the layer II and IV seem to be weakened as well due to the effects of Cu. As a result, the inhomogeneous bond breaking occurs in the layer I, II and IV. Consequently, the corresponding stress drops rapidly above the critical strain as well. The elongations of the $d_1$ bond of the Cr-, W- and Ni-segregated GBs are provided in Figure 5.7d, 5.7e and 5.7f, respectively.

In addition, the origin of the inhomogeneous bond breaking in the Figure 5.7a and 5.7c can be understood in terms of the deformation charge density ($\Delta \rho$). $\Delta \rho$ is defined as the difference between the total electron density and the electron density associated with the unbounded atoms [150,151]. Forming chemical bonds in the interatomic regions are associated with accumulation of the valence electron density, which is reflected by a
positive value of $\Delta \rho$ [150,151]. The $\Delta \rho$ isosurface of the layer I, II and III of the Ta-segregated GB structure at critical strain (0.225) is plotted in Figure 5.8a, 5.8b and 5.8c, respectively, in a same view as Figure 5.6b. It is assumed each atomic layer equally occupies one fourth of the space of the supercell. The isosurface level is chosen to show the bonding density differs in the four (110) atomic layers. The $\Delta \rho$ isosurface plots of the Cu-segregated GB structure at critical strain (0.225) are presented by the same way in Figure 5.8e, 5.8d and 5.8f, respectively. Figure 5.8a shows ring-like bonds between the Ta atom and the surrounding Fe atoms in the layer I. In contrast, for the layer II and III, noticeable charge depletion is seen in the region around the Fe atom on the GB, as shown in Figure 5.8b and 5.8c, respectively. This implies that the $d_1$ bonds in the II and III layers are extremely weak at the critical strain. As the loading strain further increased, the bonds are easily broken, leading to a sudden structure collapse that results in the rapid drop of the stress. For the Cu-segregated GB, the charge depletions at the GB region are seen in the layer I and II, as shown in Figure 5.8d and 5.8e, respectively. It agrees well with the results in Figure 5.7c that the Cu leads to relatively weaker $d_1$ bonds in the layer I, II and IV. As a result, the inhomogeneous bond breaking happens in these layers above the critical strain.

All in all, it is found that the solute segregation could induce anisotropic distribution of the electron density in the region near the GB, which leads to variant strengths of the $d_1$ bonds in the four (110) atomic layers. When the applied strain is over the critical value, the weaker $d_1$ bonds are easily broken to leads to GB fracture. The inhomogeneous bond breaking can happen either on atomic layers without or with solute atoms, independently of the solute elements. Nevertheless, due to the crystal symmetry, the bonds breaking of the unalloyed
Fe GB is considered to be homogenous. As a result, the mechanical stability of the GB structure could be sustained for a few increases of the loading strain above the critical value.

5.4 Conclusion

In this part of the dissertation, the segregation effects of six transition metal elements (Cr, Ni, Cu, Zr, Ta and W) on the Σ3 (111)[1̅10] tilt boundary in BCC Fe are investigated systematically via first-principles calculations in terms of the GB energy, GB area, solute segregation energy and GB cohesion. The GB energy is effectively reduced by segregation of Zr and Ta, moderately by Cu and W, not significantly by Ni and Cr, which is well agreed with the experiments. It is found that the reductions in the GB energy caused by solute segregation is indeed mainly determined by the solute segregation energy, as assumed in the previous analytical thermodynamic models. Based on our first-principles calculations, the solute segregation energy is verified to be composed as a combination of the strain and chemical contributions. Even for the solute elements with large atomic volume, such as Zr and Ta, the chemical contribution to the solute segregation energy is found to be comparable to the reduction of the strain energy associated with the solute atomic size misfit. Furthermore, the embrittling-strengthening effects of the solute elements on GB cohesion are studied via first-principles tensile test. It is found that segregation of Zr, Ni and Cu decreases the GB cohesive strength, whereas Cr, Ta and W have a strengthening effect. In addition, solute segregation is found to induce inhomogeneous breaking of the atomic bonds at GB, resulting in a sudden collapse of the GB structure happening above the critical strain. The inhomogeneous bond breaking
originates from an anisotropic distribution of the valance charge density induced by solute
atoms in the GB region. Although the present work is limited to the $\Sigma 3 (111)[\overline{1}0]$ tilt
GB, the findings are expected to remain applicable to more general grain boundaries as the
average excess volumes are comparable.
Table 5.1 The computed total energies of the supercells with GB ($E_{GB}$) and without GB ($E_{Bulk}$) along with the GB area per supercell ($A_{GB}$), and GB energy ($\gamma_{GB}$) for each alloy system.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{GB}$ (eV/atom)</th>
<th>$E_{Bulk}$ (eV/atom)</th>
<th>$A_{GB}$ (Å)</th>
<th>$\gamma_{GB}$ (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Cr</td>
<td>-8.088</td>
<td>-8.196</td>
<td>55.053</td>
<td>1.505</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>-8.001</td>
<td>-8.107</td>
<td>54.939</td>
<td>1.474</td>
</tr>
<tr>
<td>Fe-Cu</td>
<td>-7.959</td>
<td>-8.059</td>
<td>54.879</td>
<td>1.401</td>
</tr>
<tr>
<td>Fe-Zr</td>
<td>-8.079</td>
<td>-8.166</td>
<td>55.708</td>
<td>1.212</td>
</tr>
<tr>
<td>Fe-Ta</td>
<td>-8.153</td>
<td>-8.249</td>
<td>55.283</td>
<td>1.340</td>
</tr>
<tr>
<td>Fe-W</td>
<td>-8.162</td>
<td>-8.264</td>
<td>55.086</td>
<td>1.419</td>
</tr>
</tbody>
</table>
Table 5.2 The calculated total solute segregation energy of each alloy system, and its two component parts: the strain contribution ($\Delta E_{seg}^{str}$) and chemical contribution ($\Delta E_{seg}^{chem}$). The unit for all quantities is eV.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta E_{seg}$</th>
<th>$\Delta E_{seg}^{str}$</th>
<th>$\Delta E_{seg}^{chem}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Cr</td>
<td>-0.199</td>
<td>-0.046</td>
<td>-0.153</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>-0.316</td>
<td>-0.162</td>
<td>-0.155</td>
</tr>
<tr>
<td>Fe-Cu</td>
<td>-0.572</td>
<td>-0.161</td>
<td>-0.411</td>
</tr>
<tr>
<td>Fe-Zr</td>
<td>-1.157</td>
<td>-0.570</td>
<td>-0.587</td>
</tr>
<tr>
<td>Fe-Ta</td>
<td>-0.745</td>
<td>-0.421</td>
<td>-0.324</td>
</tr>
<tr>
<td>Fe-W</td>
<td>-0.492</td>
<td>-0.315</td>
<td>-0.178</td>
</tr>
</tbody>
</table>
Table 5.3 The calculated cohesive strengths and critical strains of the clean and solute-segregated BCC Fe Σ3 GBs.

<table>
<thead>
<tr>
<th>System</th>
<th>Cohesive Strength (GPa)</th>
<th>Critical Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>22.9</td>
<td>0.250</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>23.5</td>
<td>0.225</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>22.6</td>
<td>0.225</td>
</tr>
<tr>
<td>Fe-Cu</td>
<td>21.3</td>
<td>0.225</td>
</tr>
<tr>
<td>Fe-Zr</td>
<td>21.2</td>
<td>0.200</td>
</tr>
<tr>
<td>Fe-Ta</td>
<td>23.5</td>
<td>0.225</td>
</tr>
<tr>
<td>Fe-W</td>
<td>24.3</td>
<td>0.250</td>
</tr>
</tbody>
</table>
**Figure 5.1** Schematic structures of the constructed supercells: (a) $\Sigma 3 \ (111)[1 \bar{1} 0]$ tilt grain boundary (b) bulk reference (BCC structure). The atomic sites for substituting solutes are marked by red. Each supercell contains 96 atoms in total. Both of the cell have an initial size of $2[1 \bar{1} 0]_{\text{BCC}} \times 4[111]_{\text{BCC}} \times [11\bar{2}]_{\text{BCC}}$ with respect to the BCC lattice index.
Figure 5.2 The relative changes of the GB energy, $\eta_x$, and the GB area, $\lambda_x$, with respect to the unalloyed GB. The relative changes of the GB area are neglectable compared to the relative changes of GB energy caused by segregations.
Figure 5.3 $\Delta E_{str}^{seg}$ plotted as a function of the atomic size misfit. It is found that the magnitude of the strain contribution ($\Delta E_{seg}^{str}$) increases with the solute atomic size misfit.
Figure 5.4 The total solute segregation energy ($\Delta E_{\text{seg}}$) vs. its strain contribution ($\Delta E_{\text{seg}}^{\text{str}}$):

$\Delta E_{\text{seg}}$ becomes more negative monotonically as the magnitude of $\Delta E_{\text{seg}}^{\text{str}}$ increased, despite of the discrepancy of Cu segregation.
Figure 5.5 Ideal tensile strain-stress curves of the unalloyed GB and solute-segregated GB structures. The open symbols correspond to the calculated stresses of collapsed GB structures which have not been fully relaxed.
Figure 5.6 (a) Schematic structure of the supercell with GBs in the view of [111]_{BCC} direction. The supercell is composed by four (110)-atomic layers in an ‘ABAB…’ stacking sequence. (b) Schematic structure of the layer I in Figure 5.6a. Five atomic bonds (labeled by dashed arrows) are chosen to investigate the GB fracture path. (c) Elongations of the five atomic bonds in Figure 5.6b as a function of loading strain.
Figure 5.7 Elongation of the $d_1$ bond in each (110) atomic layer as a function of loading strain. (a) Ta-segregated GB; (b) Zr-segregated GB; (c) Cu-segregated GB; (d) Cr-segregated GB; (e) Ni-segregated GB; (f) W-segregated GB.
Figure 5.8 Deformation charge density ($\Delta\rho$) isosurface of the deformed GB structure at the critical strain. Ta-segregated GB: (a) Layer I; (b) Layer II; (c) Layer III. Cu-segregated GB: (d) Layer I; (e) Layer II; (f) Layer III. The isosurface value is set to be 0.0055 eV/Å$^3$. 
Chapter 6

Nano-sized Superlattice Clusters in
Mechanically Alloyed Fe Alloys

6.1 Introduction

Creating and maintaining precipitates coherent with the host matrix, under service conditions is one of the most effective approaches for successful development of alloys for high temperature applications; prominent examples include Ni- and Co-based superalloys and Al alloys [16,46,49–51]. While ferritic alloys are among the most important structural engineering alloys in our society, no reliable coherent precipitates stable at high temperatures have been found for these alloys. BCC-Cu precipitates in the Fe-Cu system and β’ (NiAl-type) precipitates in the Fe-Ni-Al system have been explored via aging due to their lattice coherency with the BCC α-Fe matrix. Unfortunately, it was found that BCC-Cu easily transforms to FCC at 550 °C, inducing harmful brittleness [52]. Likewise, the rapid decrease of yield strength around 600 °C and high coarsening rates impede the application of NiAl-strengthened ferritic alloys at high temperatures [53,152].

In contrast to conventional aging methods, mechanical alloying provides alternative possibilities in the search and creation of precipitates, because of its capability to synthesize
highly supersaturated solid solutions and metastable intermetallics [55,56]. It may be noted that these metastable phases may not be accessible from equilibrium processing routes. One example is the oxide dispersion strengthened (ODS) steels produced through mechanical alloying of an alloy and oxide powders [153,154]. The subsequent reactions between the alloy and oxide result in the formation of complex nanoclusters and nanoparticles, whose atomic structures are intriguing and being actively investigated [153,155]. In this part of the dissertation, we show the discovery of a new, oxygen-enriched, nano-sized superlattice (NSS) clusters (2-5 nm) in ball-milled Fe and Fe alloys which maintain coherency and fine sizes up to at least 913 °C, though an investigation combined experimental measurements and first-principles calculations. Being fully coherent with the $\alpha$-Fe matrix, the NSS clusters have given rise to an additional strengthening for these Fe alloys, likely similar in nature to the aforementioned Ni- and Al-based alloys. Since the electron diffraction pattern inducted by the NSS phase does not correspond to any of the known equilibrium Fe oxide phases, its crystal structure and thermodynamic stability are further investigated via first-principles calculations. The experimental measurements and characterizations in this part of work have been performed by our collaborators at the US Army Research Laboratory and North Carolina State University.

6.2 Experimental methods

Sample Preparation: 99at.% Fe-1at.% Zr was mechanically alloyed from elemental powders via high-energy ball milling in a SPEX 8000 shaker mill. Milling vials
were carefully prepared in an ultra-high purity argon atmosphere to avoid excessive oxygen contamination. Milling was performed for 24 hours with a 10:1 ball to powder mass ratio. Control samples with no added Zr were also prepared to understand the role of Zr in the hardening and microstructural evolution. Samples were annealed in a standard tube furnace with an Ar-2% H₂ gas mixture. Milling and annealing procedures were the same as described in Reference 22.

**Transmission Electron Microscopy:** The microstructure of the samples was examined by transmission electron microscopy (TEM). Most TEM samples were prepared by focused ion-beam (FIB) milling to minimize the sample volume and thus magnetic interactions with the electron beam. (To preclude the possibility of FIB-induced artifacts from Ga implantation, control samples were also prepared by mechanical polishing the samples to 20-30 μm, followed by ion milling at low temperature to perforation. No significant differences between the differently prepared specimens were observed.) The TEM characterization was performed using a JEOL 2010F field-emission TEM operated at 200 kV and equipped with a scanning TEM (STEM) system, an energy dispersive x-ray spectroscopy (EDS) system (Oxford), and a Gatan Enfina electron energy loss (EEL) spectrometer. A JEOL 2000FX TEM microscope operated at 200 kV was used for large-angle tilting of the samples to obtain SAED patterns for multiple zone axes.

### 6.3 Computational details

The first-principles calculations in this part of dissertation are performed using the projector augmented wave method (PAW) [57,101] based Vienna ab-initio Simulation
Package (VASP) [57]. Three different exchange-correlation functionals have been applied: (i) the general gradient approximation by Perdew, Burke, and Ernzerhof (PBE) [76]; (ii) the hybrid density functional Hartree-Fock (HF) method by Hey-Scuseria-Ernzerhof (HSE06), which is mixed by 25% of the exact HF exchange and 75% of the PBE exchange-correlation functional [73,74,156]; (iii) the hybrid functional HSEsol, which has the same form as HSE06, but is based on the PBEsol functional [77] for the semi-local exchange and correlation part [72]. To increase the accuracy of the calculation, the plane wave energy cutoff is increased by a factor of 1.3 times the maximum energy of the pure elements. The structures are relaxed by implementing the Methfessel-Paxton method in order to calculate the forces acting on the atoms [100]. The atomic positions, volume, and cell shape of the proposed structures are relaxed with respect to all degrees of freedom by using high accuracy, spin-polarized calculations. The contour plots of the differential charge density were generated using VESTA [102,103]. In order to calculate the formation energy of the proposed Fe$_3$O structure, BCC-Fe, HCP-Zr, and O$_2$ molecule are also relaxed by VASP to obtain the ground state energy. The k-point grid was optimized for each calculation in order to achieve compromise between computing time and accuracy. For proposed Fe$_3$O and (Fe,Zr)$_3$O structure, a 20×20×20 grid is applied for the calculation based on PBE and a 9×9×9 grid is applied for both HSE06 and HSEsol. The k-point grids of BCC-Fe calculations are 20×20×20 for PBE and 11×11×11 for HSE06 and HSEsol. For HCP-Zr, 24×24×15 grid is chosen for PBE calculations and 11×11×6 for HSE06 and HSEsol. All the calculations of single oxygen atom and O$_2$ molecule are relaxed by implementing Gamma centered scheme with k-meshes of 1×1×1. Multislice simulations of diffraction
pattern and HRTEM images for the proposed structure model were carried out using JEMS software.

6.4 Results and discussion

6.4.1 Hardness anomaly

*Hardness data are measured by collaborator Kristopher Darling at Army Research Lab*

The Vickers microhardness versus annealing temperature of the high-energy ball milled Fe (unalloyed Fe) and Fe-1at% Zr samples, measured in our prior studies [22], is shown in Figure 6.1a and 6.1b. It is commonly accepted that the hardness of these alloys is dominated by the effects of grain boundary strengthening [22]. However, the substantial hardness difference between the Hall-Petch predictions for the ball milled BCC \( \alpha \)-Fe [21] and the experimental observations indicate that there should be additional mechanisms at play. This is particularly evident for samples that have been annealed between 530 and 913 °C. At a grain size of 7 \( \mu \)m, the hardness of the unalloyed Fe sample is close to three times of the value predicted based on the Hall-Petch relation (Figure 6.1a). This particular strengthening phenomenon can be preserved to some extent even after annealing at 1173 °C for one hour (Figure 6.1b) in the Fe-1at% Zr sample. Such an observation signifies that this strengthening phenomenon is enhanced by alloying with Zr and persists despite being exposed to high homologous temperatures, thereby displaying a significant increase in thermal resistance.
6.4.2 Structural and chemistry information of the NSS phase

*TEM, EELS and EDS characterizations are performed by collaborator Jing Li at North Carolina State University*

The microstructures of the unalloyed Fe and Fe-1at% Zr samples, which were annealed at 913 °C for one hour, were analyzed by transmission electron microscopy (TEM). Energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) were performed on samples for composition analysis. The EELS results revealed that surface oxides existed on both the Fe-1at.%Zr and unalloyed Fe TEM samples, which has the structure of Spinel Fe₃O₄ as identified by selected area electron diffraction (SAED).

Further scrutinizing the SAED patterns of the α-Fe matrix, e.g., Figure 6.2a (unalloyed Fe sample), reveals an additional set of reflections (marked with an orange circle) corresponding to α-Fe forbidden {100} reflections. In fact, the presence of these α-Fe {100} forbidden reflections are consistently observed in the α-Fe <100> SAED patterns for both unalloyed Fe and Fe-1% Zr samples. Given the existence of the surface spinel Fe-oxides, it is important to note that the observed α-Fe {100} forbidden reflections are a bulk phenomenon and cannot be attributed to surface Fe oxides. These additional reflections also do not match the structure of any other existing Fe oxides. They are believed to have come from a superlattice ordering in the α-Fe matrix as the ordering breaks the translational symmetry of the BCC crystal lattice. By using the {100} forbidden reflections in Figure 6.2a to obtain a TEM dark field (DF) image, the morphology, size, and distribution of the superlattice regions reveal a random dispersion of equiaxed nano-clusters with a size range of 2-5 nm, as shown in Figure 6.2b. The spatial dispersion of the clusters is at the same
length scale. Figure 6.2c shows the high resolution TEM (HRTEM) image of the unalloyed Fe sample along the [001] zone-axis. It is clearly shown that the nano-clusters have a perfect ordered superlattice structure in the \( \alpha \)-Fe matrix. A dispersed superlattice phase with similar size and distribution was also observed in the Fe-1 at.% Zr sample.

To further investigate the chemistry of the NSS clusters in the ball-milled Fe sample, EELS was performed. The nano-sized TEM beam was placed on the individual NSS clusters and on the surrounding \( \alpha \)-Fe matrix (as shown in Figure 6.2c), respectively. Figure 6.3 shows a comparison of the EELS spectra for the O K-edge from the NSS clusters and from the adjacent \( \alpha \)-Fe matrix. It is seen that the net intensity of the O K-edge of the NSS clusters is evidently higher than that of the adjacent \( \alpha \)-Fe matrix, revealing O-enrichment in these NSS clusters. The chemistry of the NSS clusters in the Fe-1 at.% Zr sample is also investigated. A Zr elemental map in the Fe-1 at.% Zr sample, recorded in STEM/EDS mode with a probe size of 1 nm, is presented in Figure 6.4a. The blue regions (Zr-enriched) are found to be about 5 nm, the same as the size of the NSS clusters revealed by a dark-field image in Figure 6.2b, which indicates enrichment of Zr in the clusters. Figure 6.4b and 6.4c show EDS spectra from a Zr-enriched cluster (higher Zr-L peak) and the Fe matrix (almost no Zr-L peak), respectively. Based on the EDS analysis using Zr-K and Fe-K peaks (not shown), the concentration of Zr in the NSS clusters is around 6.0 at.\%, substantially higher than the equilibrium solubility of Zr in \( \alpha \)-Fe [157]. Furthermore, the intensity of oxygen in Figure 6.4b is nearly two times higher than that in Figure 6.4b, indicating that oxygen is also enriched in the NSS clusters for the Fe-1 at.% Zr sample.
6.4.3 Crystal structure and phase stability of the NSS phase

Since the diffraction pattern caused by the NSS clusters does not correspond to any of the known equilibrium Fe oxide phases, the crystal structure and thermodynamic stability of the NSS phase need further investigations. The superlattice reflections are observed in both unalloyed Fe and Fe-1at.% Zr samples; as such, the NSS clusters are more likely to arise from oxygen ordering, rather than other ordering mechanisms, such as Zr ordering. Based on the above observations, we propose the NSS phase has a D0$_3$ (A$_3$B) structure, where Fe occupies the A sites and O occupies the B sites to form a Fe$_3$O unit cell (Figure 6.5a). Similar crystal structure exists in ferritic intermetallics (Fe$_3$Al and Fe$_3$Si) [158,159] and other BCC metal oxides (Mo$_3$O) [160]. The proposed structure model could be thought of as a FCC superlattice ordering in the BCC matrix. The FCC unit cell consists of eight ($2 \times 2 \times 2$) $\alpha$-Fe unit cells, in which the Fe atoms on the corners and the face-centered sites are replaced by O atoms.

Figure 6.5b shows the simulated [001] diffraction pattern of the Fe$_3$O structure. As expected, because of the oxygen ordering, additional superlattice {100} reflections appear on a typical BCC [001] diffraction pattern, which is in good agreement with the observations in Figure 6.2a. Moreover, as shown in Figure 6.5c, the simulated Fe$_3$O HRTEM image along the [001] zone-axis (inset in Figure 6.5c) is consistent with the experimentally observed one in the unalloyed Fe. Here, the [001] zone axis is particularly useful and critically important for identifying the ordered structure of NSS clusters because the corresponding reflections cannot be obstructed by neither the double diffraction nor the reflection from surface oxides. In addition, the simulated SAED patterns of the proposed
Fe₃O structure along other zone axis are also compared with corresponding patterns of the BCC Fe matrix, as shown in Figure 6.6. Comparing Figure 6.6a with 6.6b indicates that the Fe₃O structure will not create additional reflection on the [113̅] BCC Fe SAED pattern. This is in good agreement with experimental observations. Comparing Figure 6.6c with 6.6d, it is shown that the Fe₃O structure creates extra superlattice reflections on the BCC Fe [112̅] SAED pattern. However, as seen from Figure 6.6e, the diffraction pattern of Fe₃O along [112̅] direction are either overlap (red circles) or are very close (red dots) to those of the surface Fe₃O₄. It is reasonable to assume that due to the existence of the [101̅] SAED pattern of surface Fe₃O₄ along this zone axis, the extra superlattice reflections of [112̅] Fe₃O may be very dim and could not be observed.

In order to validate the phase stability of the proposed crystal structure (D₀₃ structure) and its coherency with BCC Fe matrix, first-principles calculations are performed to calculate the equilibrium lattice parameters and ground state energies. As shown in previous calculations, the two common DFT electron exchange-correlation functionals, the local-density (LDA) and the generalized gradient approximation (GGA-PW91), lead to considerable errors in calculated redox energies, especially for 3d transition metals oxides [161,162]. The errors can be attributed to self-interaction error in electron density during electrons transfer and localization [161]. It is found such errors can be corrected by using the DFT+U approach and modifying the ground state energy of O₂ molecule based on experimental binding energy [161]. The empirically determined U parameter is chosen by comparing with various experimental data, which means such method can only be applied to oxides which have available experimental measurements [161,163].
The hybrid exchange-correlation functional, HSE06, has been shown to reproduce accurately redox energies of transition metal oxides [164,165]. In the hybrid approach, Hartree-Fock exchange is taken into account to partially cancel the electron self-interaction error mentioned above. In addition, HSE06, unlike the U parameter approach, is a parameter free functional that can accurately study oxides binding for which no experimental measurements exit. Unfortunately, HSE06 was found to have tendency to overestimate lattice constants, which is pronounced in various metal elements, including Fe [166,167]. Additionally, the atomization energies of transition metals exhibit significantly increased errors compared to PBE. To further correct the errors of lattice parameter and atomization energies in the HSE06 functional, another hybrid functional, HSEsol, was introduced recently [72]. The HSEsol functional has the same form as HSE06, but use the PBEsol functional for the semi-local exchange and correlation part instead of PBE. Compared to HSE06, HSEsol exhibits better predictions of lattice parameters for some transition metals (Cu, Pd, Ag and Rh) [72]. However, it has not been demonstrated that HSEsol can also reproduce redox energies of transition metals as well as HSE06. Therefore, in order to study the proposed Fe$_3$O structure comprehensively and systematically, these three functionals, PBE, HSE06 and HSEsol, are all employed here.

The equilibrium state of the pure Fe and Zr, and proposed D0$_3$ structure in the present work, $E(V)$, is determined by fitting the total energy vs. volume based on the four-parameter Birch-Murnaghan equation of state (EOS) [61]. For the NSS phase contains Zr, one Zr atom is added into the Fe$_3$O supercell to replace one Fe atom for the sake of consistency with the experimental composition. The atomic positions of Zr are considered for two possible cases due to the symmetry: Zr occupies the first nearest neighbor site
(FNS) or the second nearest neighbor site (SNS) with respect to the oxygen atom. In order to validate the calculations of redox energies, α-Fe₂O₃ is also included.

The lattice parameters of BCC-Fe, HCP-Zr, α-Fe₂O₃, Fe₃O and (Fe,Zr)₂O calculated from different exchange-correlation functionals are summarized in Table 6.1. Experimental data and other first-principles calculations results are also included for comparison. In addition, for BCC-Fe, HCP-Zr and α-Fe₂O₃, we report the corresponding relative error of calculated results with respect to the experimental values. Table 6.1 reveals that both PBE and HSEsol provide good predictions of the lattice parameters of BCC-Fe, HCP-Zr and α-Fe₂O₃, giving errors within 1% compared to experimental data. The prediction of HCP-Zr and α-Fe₂O₃ achieved by HSE06 is also in good agreement with experiments. However, for BCC-Fe, HSE06 significantly overestimates the lattice parameter, which is 2.0% larger than experimental values. Similar result was reported in other calculations as well [166]. In order to investigate the coherency between the proposed Fe₃O structure and the BCC-Fe matrix, we calculate the lattice mismatch of Fe₃O with respect to both experimental and calculated lattice parameters of BCC-Fe. The results are listed in Table 6.1. As seen from the table, very small lattice mismatch is achieved by all three functionals, with respect to experimental lattice parameter of BCC-Fe. The average lattice mismatch is about -0.7%, which indicates a good coherency between the Fe₃O and BCC-Fe, in agreement with the HRTEM observation. The values of lattice mismatch with respect to the calculated lattice parameter are very different. For the PBE functional, the lattice mismatch is as small as 0.3%, while HSE06 gives a large mismatch of -2.1%, which could be attributed to the bad estimation on the lattice parameter of BCC-Fe.
Table 6.2 reports the ground state energies ($E_0$) of a single O atom and the O$_2$ molecule calculated by using PBE, HSE06 and HSEsol functionals. Based on the ground state energy, the binding energy ($\Delta E$) of the O$_2$ molecule is calculated and compared with the experimental value. As seen from the table, PBE predicts a binding energy of -6.04eV, which is considerably higher than the experimental value. Similar results were also reported in the literatures [161,168]. HSEsol also overestimates the binding energy of O$_2$ molecule by 0.44eV. In contrast, the HSE06 calculation yields a binding energy of -5.15 eV, in much better agreement with experiments compared to the predictions of PBE and HSEsol. In order to eliminate the effects of such overestimations on the further calculations of formation enthalpies, we also give the corrected ground state energy of O$_2$ molecule which is modified based on the experimental binding energy.

Two types of 0K formation enthalpies of $\alpha$-Fe$_2$O$_3$, the proposed Fe$_3$O and (Fe,Zr)$_3$O structures with respect to BCC-Fe, HCP-Zr and the O$_2$ molecule are listed in Table 6.3. The $\Delta H$ is calculated by using the ground state energy of O$_2$ molecule from direct DFT calculations and the $\Delta H^{\text{corrected}}$ is based on the corrected ground state energies of the O$_2$ molecule shown in Table 6.2. As seen from Table 6.3, PBE significantly underestimates the formation enthalpies of $\alpha$-Fe$_2$O$_3$ which confirms the previous argument in the beginning of this chapter. Even with the ground state correction for the O$_2$ molecule, the formation enthalpy is still 18.3 kJ/mol-atom lower than the experimental value. In contrast, the HSE06 functional provides much better prediction of the formation enthalpy of $\alpha$-Fe$_2$O$_3$ as expected. Besides, the HSEsol functional overestimates the formation enthalpies of $\alpha$-Fe$_2$O$_3$ for both corrected and uncorrected cases. Therefore, it can be concluded that the HSE06 functional would provide more reliable formation enthalpies of the proposed Fe$_3$O
and (Fe,Zr)$_3$O structures rather than the other two functionals. Although the 0 K enthalpy of formation is as high as 39.0 kJ/mol-atom, it is entirely possible to produce this non-equilibrium oxygen ordering structure at the nano-scale through mechanical alloying, which has been widely used to synthesize non-equilibrium alloy phases [55,56]. For example, the meta-stable BCC W-Cu solid solution, which has a positive enthalpy of formation around 35 kJ/mol-atom, was synthesized via mechanical alloying processing [169].

In addition, it is revealed that the formation enthalpy of (Fe,Zr)$_3$O (FNS) structure is much lower than that of the (Fe,Zr)$_3$O (SNS) structure, which means that the former structure is more stable at equilibrium state. However, given that the FNS structure has larger lattice parameter than the SNS structure while constrained in BCC-Fe matrix, it is important to compare their energies under constrained conditions. Constrained state energies could be achieved via the E-V fittings which provides the volume dependence of the total energy. It is found that the constrained state energy of the FNS structure is still much lower than it of the SNS structure. Therefore, it is proposed that the Zr will prefer to occupy the nearest neighbor rather than second nearest neighbor sites of oxygen.

**6.4.4 Effects of Zr on the stability of the NSS phase**

In addition to elucidating the atomic structure of NSS clusters, it is important to understand the role of Zr in stabilizing these clusters, as Zr is observed to enrich the nano-clusters, and the strengthening induced by the NSS clusters is better preserved in Fe-1at% Zr samples after high temperature annealing. After fully relaxing the supercell, the
deformation electron density in the (1 ̅1 0)-plane, represented by the charge density difference for the fully relaxed structure with and without self-consistent calculations, are plotted in Figure 6.7a and 6.7b for the Fe₃O and Fe-O-Zr supercells, respectively. The electron density between Fe and O is low in both figures, indicating that the interactions between them are weak. However, the charges of Zr and O exhibit significant delocalization and polarization along the [111] direction, implying strong bonding between Zr and O. This explains the co-enrichment of Zr and O in the EDS data as Zr and O prefer coupling with each other to form strong chemical bonds. Considering that the NSS clusters are in a metastable state in Fe-matrix, they start to decompose at high temperatures. As shown in Figure 6.1a, after annealing at 1173 °C, the hardness enhancement due to the presence of nano-clusters in pure Fe is practically eliminated since the clusters are probably decomposed by annealing. However, because of the strong chemical bonds between Zr and O, the NSS clusters could be further stabilized at higher temperatures by Zr, which are found to enrich in these nano-clusters. As a result, the Fe-1at.% Zr samples can retain the higher-than-predicted hardness even after annealing at high temperatures.

6.5 Conclusion

A metastable Fe₃O phase, in the form of nano-sized superlattice (NSS) clusters, is produced by mechanical alloying of Fe powders containing surface oxides. Originating from an ordering of oxygen in the BCC Fe-matrix, the Fe₃O phase is fully coherent with the BCC Fe matrix and forms ordered superlattice clusters with sizes on the order of 2 to 5 nm. As a result, a new, nano-scale coherent precipitate strengthening phenomenon results
in this ball-milled BCC Fe. An enhancement of hardness is observed in the samples with submicro- or micrometer grain sizes. The phase stability and lattice parameters of the proposed Fe₃O phase are further investigated via first-principles calculations. The predicted lattice parameter of the relaxed supercell shows an average lattice mismatch of -0.7% when compared to the initially set value, indicating a good coherency with the BCC matrix. It is found that HSE06 functional would provide more reliable formation enthalpies of the Fe₃O phases. The positive value of formation enthalpy indicates that the Fe₃O phase has a non-equilibrium oxygen ordering structure which is produced by high energy mechanical alloying at the nano-scale. The experimentally observed co-enrichment of Zr and O is explained by the analysis of the electronic structures mapped in the NSS phase. The strong chemical bonds between Zr and O also explains why the NSS phase could be further stabilized at higher temperatures by Zr.
Table 6.1 Lattice parameters of BCC-Fe, HCP-Zr, α-Fe₂O₃, Fe₃O and (Fe,Zr)₃O calculated by the PBE, HSE06 and HSEsol functionals. The other first-principles calculations results by using same functionals are also included. The unit of lattice parameters is Å. For BCC-Fe, HCP-Zr and α-Fe₂O₃, the comparison with experimental lattice parameters is given in terms of the relative error. The lattice mismatch is calculated as the relative difference between the lattice parameter of Fe₃O and the two times of the BCC-Fe lattice parameter.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Zr</th>
<th>α-Fe₂O₃</th>
<th>Fe₃O</th>
<th>(Fe,Zr)₃O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
<td>a</td>
<td>c</td>
<td>SNS</td>
</tr>
<tr>
<td>Expt.</td>
<td>2.861ᵃ</td>
<td>3.230ᵇ</td>
<td>5.141ᵇ</td>
<td>5.035ᶜ</td>
<td>13.747ᶜ</td>
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<tr>
<td></td>
<td>2.832</td>
<td>3.233</td>
<td>5.147</td>
<td>5.045</td>
<td>13.801</td>
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<tr>
<td>PBE</td>
<td>2.832ᵈ</td>
<td>3.240ᵉ</td>
<td>5.178ᵉ</td>
<td>5.016ᶠ</td>
<td>13.876ᶠ</td>
</tr>
<tr>
<td></td>
<td>-1.0%</td>
<td>+0.1%</td>
<td>+0.1%</td>
<td>+0.2%</td>
<td>+0.4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSE06</td>
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<td>3.255</td>
<td>5.160</td>
<td>5.035</td>
<td>13.723</td>
</tr>
<tr>
<td></td>
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<td>5.035ᶠ</td>
<td>13.763ᶠ</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>+2.0%</td>
<td>+0.6%</td>
<td>+0.3%</td>
<td>0.0%</td>
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<tr>
<td>HSEsol</td>
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<td>5.093</td>
<td>5.009</td>
<td>13.652</td>
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<tr>
<td></td>
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<td>-0.4%</td>
<td>-0.9%</td>
<td>-0.5%</td>
<td>-0.7%</td>
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</tbody>
</table>

ᵃ Experimental measured lattice parameter of BCC-Fe at 93K [170]
b Experimental measured lattice parameter of HCP-Fe at 4.2K [171]
c Experimental measured lattice parameter of α-Fe₂O₃ at 273K [172]
d  Calculated lattice parameter of BCC-Fe by other first-principles calculations [166,173]

e  Calculated lattice parameter of HCP-Zr by other first-principles calculation [174]

f  Calculated lattice parameter of $\alpha$-Fe$_2$O$_3$ by other first-principles calculation [175]
Table 6.2 The ground state energies ($E_0$) of single O atom and O$_2$ molecule, and the binding energy ($\Delta E$) of O$_2$ molecule calculated by using PBE, HSE06 and HSEsol functionals. The differences between the calculated binding energies and experimental data are listed below the $\Delta E$. The corrected ground state energy of the O$_2$ molecule is calculated via $E_{0\text{corrected}} = 2E_0(\text{O atom}) + \Delta E_{\text{Expt.}}$. The unit of all the data in Table 6.2 is eV.

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
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<th>HSEsol</th>
<th>Expt.</th>
</tr>
</thead>
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<tr>
<td>$E_0$ (O atom)</td>
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<td>-5.46</td>
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<tr>
<td>$E_0$ (O$_2$ molecule)</td>
<td>-9.86</td>
<td>-17.04</td>
<td>-16.48</td>
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</tr>
<tr>
<td>$\Delta E$</td>
<td>-6.04</td>
<td>-5.15</td>
<td>-5.57</td>
<td>-5.13$^a$</td>
</tr>
<tr>
<td>$E_{0\text{corrected}}$ (O$_2$ molecule)</td>
<td>+0.91</td>
<td>+0.02</td>
<td>+0.44</td>
<td></td>
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</table>

$^a$ Reference [143]
Table 6.3 0K formation enthalpies of α-Fe₂O₃, the proposed Fe₃O and (Fe,Zr)₃O structures with respect to BCC-Fe, HCP-Zr and O₂ molecule. The ΔH is calculated by using the ground state energy of O₂ molecule from direct DFT calculations and the ΔH_{corrected} is calculated based on the corrected ground state energies of O₂ molecule in Table 6.2. The unit of all the formation enthalpies is kJ/mol-atom.

<table>
<thead>
<tr>
<th></th>
<th>Fe₂O₃</th>
<th>Fe₃O</th>
<th>(Fe,Zr)₃O (SNS)</th>
<th>(Fe,Zr)₃O (FNS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔH</td>
<td>ΔH_{corrected}</td>
<td>ΔH</td>
<td>ΔH_{corrected}</td>
</tr>
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<td></td>
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<td>29.4</td>
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<tr>
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<td>39.0</td>
<td>38.4</td>
</tr>
<tr>
<td>HSEsol</td>
<td>-177.9</td>
<td>-190.7</td>
<td>38.7</td>
<td>33.5</td>
</tr>
</tbody>
</table>

² Reference [143]
Figure 6.1 Indentation hardness of (a) unalloyed Fe (orange) and (b) Fe-1at.% Zr (blue) versus annealing temperature for 1 hour annealing time. The solid lines indicate the observed hardness and the dotted lines indicate the hardness predicted by the Hall-Petch relationship for ball-milled Fe given by Jang and Koch [21]. Hardness and grain size data are by Darling et al. [22]. The asterisk (*) indicates the 913 °C annealed samples analyzed by TEM in the present work.
Figure 6.2 SAED pattern, dark and bright field image of the pure Fe sample. (a) SAED pattern by tilting BCC Fe to [001] showing {100} superlattice reflections (marked with circle). (b) Dark-field image using the 010 superlattice reflection marked in (a) showing dispersed phase 4.4 ±0.9 nm in size. (c) [001] HRTEM image showing clustering of ordered superlattice phase (2-5 nm in size). Dashed lines mark approximate boundaries of a few clusters.
Figure 6.3 Comparison of the EELS O K-edge spectra from an NSS cluster (blue solid line) and the adjacent $\alpha$-Fe matrix (red dash line) in the unalloyed Fe sample, revealing the oxygen enrichment of the NSS cluster.
Figure 6.4 (a) Zr elemental map in a grain of the Fe-1at.% Zr alloy recorded in STEM/EDS mode (probe size: 1 nm) showing Zr-enriched clusters with a size of ~ 5 nm. (b) EDS spectrum from Zr-enriched cluster showing a high oxygen content. (c) EDS spectrum from Fe matrix showing a lower oxygen content and no Zr.
Figure 6.5 (a) Proposed Fe₃O unit cell which contains 12 Fe atoms and 4 O atoms and has a space group symmetry of Fm\bar{3}m. (b) Simulated [001] diffraction pattern of the proposed Fe₃O structure (here Fe₃O \{020\} reflections correspond to BCC \{010\} superlattice reflections). (c) Experimentally observed [001] HRTEM image (pure Fe sample) compared with the simulated HRTEM image of [001] projection of the proposed Fe₃O structure (inset within an orange dotted box), showing good agreement.
Figure 6.6 Simulated SAED patterns for the proposed Fe₃O structure along different zone axes compared with those of BCC Fe. (a) Simulated SAED patterns for Fe₃O along the [113] zone axis. (b) Simulated BCC Fe pattern along the [113] zone axis. (c) Simulated Fe₃O pattern along the [112]. (d) Simulated BCC Fe pattern along the [112] zone axis. (e) Simulated SAED pattern for surface Fe₃O₄ along the [10\bar{1}] zone axis. The red circles and dots mark the positions of the [112] reflections of Fe₃O [copied from (c)].
Figure 6.7 (a) Differential charge density map of the Fe₃O unit cell in (1 1 0) plane without Zr; (b) one Fe atom replaced by Zr. The unit of charge density is e/Å³.
Chapter 7

Conclusion and Future Work

7.1 Conclusion

In this dissertation, the effects of alloying elements on the elastic and plastic properties of W-based alloys, as well as the solute segregations on grain boundaries and a new precipitate phase in Fe-based alloys, are systemically studied via DFT based first-principles calculations. The calculations are coupled with novel methods and models, such as the flexible boundary condition method, solute-dislocation solid-solution model and coincidence sites lattice model. This work provides an in-depth understanding of the effects of crystalline defects (i.e., solutes, dislocations and grain boundaries) and precipitate phases on the mechanical and thermodynamic properties of W-based alloys and Fe-based alloys. The results and conclusions can be used as guidance for the future design of these alloys for applications at elevated temperatures. The main conclusions include:

1. The effects of alloying elements on the elastic properties of BCC W are investigated systematically as a function of temperature, including isothermal and isentropic elastic stiffness, bulk modulus, shear moduli, Young’s modulus, and elastic anisotropy. Nineteen transition metal alloying elements are considered: Ti, V, Cr,
Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. Based on the first-principles results at 0 K, it is found that: (i) the bulk modulus of the dilute W-X alloys decreases with increasing equilibrium volume, particularly for alloying elements in the same period; (ii) the earlier and later transition elements (e.g., Y, Zr and Pd) have stronger effects on the shear modulus than the other elements (e.g., Cr and Mo) which have the same number of valence electrons as W; and (iii) the largest decrease of W elasticity is due to the alloying element Y. The alloy effects on the elastic properties of W are traceable from the redistribution of electronic charge densities caused by the addition of alloying elements in the parent lattice.

2. The solute-induced strength softening and hardening in BCC W has been systematically studied via directly computing the solute-dislocation interaction by first-principles approach. Twenty-one alloying elements are considered: Al, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. The main findings in this part of work are summarized as follows: (i) the solute elements in the IV and V group have weakly repulsive interactions with the $\frac{1}{2}<111>$ screw dislocation, while other solute elements (including Al) show attractive interactions with the dislocation as reflected by the negative interaction energies; (ii) the solutes affect the double-kink nucleation by modifying the enthalpy barrier locally and changing the stress scale of the nucleation barrier globally; (iii) the kink migration is limited by the solute pining effects from the largest solute cluster along the dislocation line; (iv) due to the negative solute-dislocation interaction energy and Peierls misfits, small addition of the solute elements in the VI, VII and VIII group and Al could soften BCC W by promoting the nucleation of double kinks; (v)
among the examined solute elements which have softening effects, Al and Mn are proposed to be the most promising alternatives to Re to improve the ductility of BCC W at low temperatures.

3. The segregation effects of six transition metal elements (Cr, Ni, Cu, Zr, Ta and W) on the Σ3 (111)[110] tilt boundary in BCC Fe are investigated comprehensively via first-principles calculations in terms of the GB energy, GB area, solute segregation energy and GB cohesion. It is found that the solute segregation energy is composed as a combination of the strain and chemical contributions. Even for the solute elements with large atomic volumes, such as Zr and Ta, the chemical contribution to the solute segregation energy is found to be comparable to the reduction of the strain energy associated with the solute atomic size misfit.

4. The effects of the solute elements on GB cohesion are studied via first-principles tensile test. It is found that segregation of Zr, Ni and Cu decreases the GB cohesive strength, whereas Cr, Ta and W have strengthening effects. The solute segregations are found to induce inhomogeneous breaking of the atomic bonds at GBs, resulting in a sudden collapse of the GB structure above a critical strain. The inhomogeneous bond breaking originates from an anisotropic distribution of the valance charge densities induced by solute atoms in the GB regions.

5. A new, nano-sized superlattice (NSS) phase, which maintains coherency with the BCC matrix up to at least 913°C, has been discovered in the ball-milled Fe alloys. As a result, a nano-scale coherent precipitate strengthening phenomenon results in these ball-milled ferritic alloys. An enhancement of hardness is observed in the samples with submicro- or micrometer grain sizes. Since the diffraction pattern
inducted by the NSS phase does not correspond to any of the known equilibrium Fe oxide phases, the crystal structure and stability of this precipitate phase is studied via first-principles approaches. Based on the calculation results, it is proposed that this phase is metastable with respect to other stable Fe oxides, and has a chemistry of Fe$_3$O and a D0$_3$ crystal structure. The experimentally observed co-enrichment of Zr and O is explained by the analysis of the electronic structures mapped in the precipitate phase. The strong chemical bonds between Zr and O also explains why the NSS phase could be further stabilized at higher temperatures by Zr.

### 7.2 Future work

In order to search for alternative elements to Re to soften W, one part of the present dissertation studies the effects of alloying elements on the both elastic and plastic properties of BCC W. However, in order to fully understand the “Re-ductilizing” effects in BCC W, some of other challenges remain to be investigated in the future.

Generally, there are two promising mechanisms to explain the “Re-ductilizing” effect: (i) solute softening in which the mobility of the $\frac{1}{2} <111>$ screw dislocation is improved by dislocation-solute interaction; (ii) changing of preferred cross-slip plane from \{110\} to \{112\} due to the core symmetry breaking so that the number of possible slip planes is increased [1,15,87,176,177]. The present dissertation has studied the former mechanism systematically and applied it to other solute elements. However, for the latter one, it is still controversial whether the preferred cross-slip planes are directly related to the dislocation core symmetry [88,89]. For example, the number of possible slip planes
may not be increased by introducing Re since the strong non-Schmid slip behavior in BCC W may make the twelve {112} planes non-equivalent under a certain stress condition. Therefore, the mechanism and origin of the non-Schmid behavior in BCC W needs further investigation, and so as the effects of Re on the non-Schmid behavior itself. In addition, the solute-dislocation interaction should be studied with more physical detail, such as its electronic origin.

In the present dissertation, only the BCC Fe has been studied in aspects of GB segregation and precipitates strengthening. For the applications at high temperatures, the ferritic alloys may go through a BCC-FCC phase transition since the transition temperature for pure Fe is only 912 °C. Therefore, the solute segregation effects studied here are expected to be further investigated for the high temperature austenite phase. The enhancement on the grain boundary stability induced by solute segregation need to be sustained after the phase transition at elevated temperatures. Similarly, the evolution of the NSS phase as function of temperature still need further probing to rationalize how the phase forms and whether the coherency is retained after the BCC-FCC phase transition.
Bibliography


VITA

Yong-Jie (Yongjie) Hu was born on April 2\textsuperscript{nd}, 1987 in Lanzhou, China. He graduated from Tsinghua University in 2010 with a B.E. degree in Materials Science and Engineering. Since 2010, he started graduate study in Tohoku University, and graduated in 2012 with a M.E. degree in Materials Science. In 2012, he joined the Phases Research Laboratory at the Pennsylvania State University towards to obtain his Ph.D. degree. During his study at Penn State, he has received the STT scholarship and the department Travel Award scholarship in 2016.

Listed below are his publications during his Ph.D. study:
