

Contents

Contents	I
List of Figures	V
List of Tables	IX
1 Introduction	1
1.1 Motivation and aims of the work	1
1.1.1 The hydrogen energy transition	1
1.1.2 Hydrogen storage in molecular state	2
1.1.3 Hydrogen storage as metal-hydrides	3
1.1.4 FeTi as solid-state hydrogen storage material	11
1.1.5 The use of computational methods for solid-state hydrogen storage: aims of this work	13
1.2 Outline of the work	14
2 Theoretical Foundations	17
2.1 Methodology overview	17
2.2 Introduction to First-Principles calculations	18
2.2.1 Quantum mechanics calculations and its use for thermodynamic modeling	18
2.2.2 Schrödinger equation and the many-body problem	20
2.2.3 The density-functional theory (DFT) and its approximations	21
2.2.4 Computational Solution, Plane Wave Basis Sets, and Pseudopotentials	26
2.3 Introduction to the Calphad Method	29
2.3.1 The Computational Thermodynamics Concept	29
2.3.2 Foundation for Equilibrium Calculations	30
2.3.3 Phase stability calculation	31
2.3.4 Gibbs Energy Models and Formalism	31
2.4 Introduction to Phase-Field modeling	36
2.4.1 Basic Phase-Field equations	36

2.4.2	The Kim-Kim-Suzuki phase-field model	39
2.4.3	Including Micromechanics	40
3	Thermodynamic Modeling of the FeTi Hydrogenation	43
3.1	Review on the thermodynamics of binary systems	43
3.1.1	Thermodynamics of Fe-H and Ti-H systems	43
3.1.2	Thermodynamics of the Fe-Ti System	43
3.2	Thermodynamic modeling of the FeTi-H system	52
3.2.1	Introduction to the FeTi-H system	52
3.2.2	Crystal structure of FeTi-based hydrides	58
3.2.3	First-principles calculations	60
3.2.4	Thermodynamic modeling	66
3.2.5	Thermodynamic assessment of model parameters	73
4	Interfacial Properties of FeTi Metal-Metal Hydride	81
4.1	Interphase boundary chemical energy	81
4.1.1	The Grand Potential approach	81
4.1.2	The Hydrogenation Reaction approach	86
4.1.3	Application of the models to the FeTi-H surfaces and interphase boundaries	88
4.2	Interphase boundary strain energy density	96
4.2.1	Fundamentals for microelasticity theory	96
4.2.2	Micromechanical analysis	97
5	Phase-Field Simulations of the FeTi Hydrogenation	107
5.1	Phase-Field Modeling the FeTi-H system	107
5.1.1	Modeling the free energy functional of the FeTi-H system	108
5.1.2	Parametrization of the interphase energy and thickness	112
5.1.3	Mobility parameters	115
5.2	Phase-Field Simulations	117
5.2.1	Simulation of the interface equilibrium between α and β phases	117
5.2.2	Simulations of the β hydride growth from super-saturated α matrix	119
5.2.3	Simulations of the FeTi alloy hydrogenation	129
5.2.4	Simulations of spinodal decomposition of the β phase	133
5.2.5	Simulations of coupled micromechanics for phase transformation	137
6	Summary and Outlook	143
6.1	Summary of the dissertation	143
6.2	Future perspectives	144

Appendices	147
A Quantum Mechanics	149
A.1 Investigation of DFT settings	149
B Thermodynamics	163
B.1 Useful Gibbs Energy Relations	163
C Phase-Fields	165
C.1 FEM solutions for phase-field problems	165
C.1.1 Theorems useful for solving the phase-field problems .	165
C.1.2 Constructing residuals	166
D Supplementary Material	171
D.1 POSCAR files	171
Bibliography	173
Acknowledgements	189