Wear by corrosion of refractory materials remain a major concern for plant operators, manufacturers of refractories, installers and refractory engineers involved in R&D and Education in this field of expertise. The entire subject will be covered in within tree volumes. The other will present an in-depth compilation of the major testing tests and characterization methods (volume 2B) and the impact of corrosion on plants availability and products quality, revealing what can be learned from post-mortem analysis, through pertinent case studies (volume 2C).

The first volume (volume 2A) on the Fundamentals is being treated at he macro-, meso- and microscopic scale, focusing on degradation mechanisms including thermal aspects; chemical aspects and transfer of materials; phase changes and mechanical aspects; and coupling between all those aspects. It does provide the readers with the conceptual tools for a clear understanding of the degradation phenomena frequently observed, providing the insights for improving the performances of those materials (inserted in complex linings) and exposed to increasingly harsh environment.

Seven authors have been recruited by FIRE, lead by J. Poirier and M. Rigaud, to cover the seven chapters: 1- Features of refractory corrosion by J. Poirier and m. Rigaud; 2- Thermodynamics by M. Rigaud, J. Smith, In-Ho Jung and J. Poirier; 3- Kinetics by Y-B Kang; 4- Wettability by N. Eustathopoulos; 5- Reactions and mechanisms of corrosion by J. Poirier; 6- Thermal, chemical and mechanical couplings by É. Blond; 7-Impact of operating conditions on refractory lining wear by J. Poirier and M. Rigaud.

The content of the book has been reviewed by fourteen fellow experts (industrials and academics) worldwide. It represents a major contribution to grasp in depth the main principles to address the major issues concerning the corrosion of refractories.
# Table of Contents

Foreword vii  
Preface viii  
The Authors xi  
F.I.R.E. xiii

## Chapter 1

**Features of refractory corrosion**

1. **Introduction** 1  
2. **Issues of refractory corrosion and industrial sectors affected** 8  
3. **Degradation factors** 12  
4. **Characteristics and durability of refractories** 18  
5. **Designing the microstructure for corrosion resistance** 19  
6. **Fundamentals and tools: thermodynamics and kinetics, wettability, post mortem examinations, experimental methods** 24  
   6.1. Thermodynamics 26  
   6.2. Kinetics 27  
   6.3. Wettability and refractory infiltration by liquids 27  
   6.4. Industrial expertise, observation of operational corrosion, “post mortem” sample examination 32  
   6.5. Laboratory study of corrosion phenomena 33  
7. **Conclusion** 37  
8. **References** 38

## Chapter 2

**Thermodynamics**

1. **Introduction** 43  
2. **Basic Knowledge of Thermodynamics** 44  
   2.1. Gibbs Energy 45  
   2.2. Stability and Equilibrium 46  
   2.3. Thermodynamics of Solutions 50
## Contents

2.4. Solubility limits  

3. **Equilibrium Diagrams**  
   3.1. Ellingham Type Diagrams  
   3.2. Area Predominance diagrams  
   3.3. Phase Diagrams of Two Components  
   3.4. Phase Diagrams of Three Components  

4. **Computational Thermodynamics**  
   4.1. Thermodynamic Packages and Databases  
   4.2. Refractory Corrosion Applications  

5. **Microstructure and phase transformation of corroded refractories explained by phase diagrams and thermodynamics**  
   5.1. Introduction  
   5.2. Microstructural transformation of phases predicted by thermodynamics  
   5.3. Crystallization paths explained by microstructures and thermodynamics  
   5.4. Corrosion of refractories interpreted by microstructures and thermodynamics  

6. References  

### Chapter 3  
**Kinetics**

1. **Introduction**  
2. **Basic knowledge of the kinetic theory**  
   2.1. Definition of reaction rate  
   2.2. Homogeneous reaction  
   2.3. Heterogeneous reaction  

3. **Experimental studies for dissolution kinetics**  
   3.1. Experimental techniques  
   3.2. Uncertainty and limit of the experimental approaches  

4. **Modeling studies for dissolution kinetics**  
   4.1. Different modeling techniques  
   4.2. Coupling with thermodynamics/phase equilibria  
   4.3. Perspective of the modeling approach  

xvi
Contents

5. Summary 180

6. References 180

Chapter 4
Wetting and infiltration of refractories by liquid metals and oxides

1. Introduction 187

2. Fundamental equations of wetting and capillarity 188
   2.1. Surface energy and adhesion energy 188
   2.2. Young and Young-Dupré equations 189
   2.3. Capillary Pressure-Laplace’s equation 192
   2.4. Effect of surface roughness and surface heterogeneities on
       the contact angle 194
   2.5. Wetting kinetics of non-reactive liquids 198

3. Data of contact angles for non-reactive liquid-solid systems 203

4. Effects of interfacial reactions 207
   4.1. Wetting with formation of a new compound at the interface 207
   4.2. Dissolutive wetting 211

5. Methods of measuring the contact angle 212

6. Infiltration 214
   6.1. Non-reactive infiltration-Thermodynamics 214
   6.2. Non-reactive infiltration-Kinetics 216
   6.3. Effects of interfacial reactions 221

7. References 226

Chapter 5
Reactions and Mechanisms of Corrosion

1. Introduction 229

2. Influence of temperature 229
   2.1. Maximum temperature of usage 229
   2.2. Effect of phase transformations 238

3. Influence of the liquid phase characteristics 242
   3.1. Slag characteristics: roles, structures and properties 243
   3.2. Marangoni Effect 258
   3.3. Transport Mechanism 260

xvii
Contents

3.4. Reaction inventory and fundamental mechanisms 271

4. Influence of the gaseous environment 297
   4.1. Corrosion by gas with formation of gaseous, liquid or solid products 297
   4.2. Fundamental mechanisms of corrosion with formation of gaseous, liquid or solid products [74] 299
   4.3. Reaction inventory and key factors of corrosion 303

5. How to limit the corrosion? (further details in volumes 2B and 2C) 328

6. References 330

Chapter 6
Thermal, chemical and mechanical couplings

1. Introduction 337

2. Definition of the System and State Variables 340
   2.1. Equilibrium, steady-state and evolution 341
   2.2. State variables 342
   2.3. Local state postulate 343

3. Balances/Conservation Laws 344

4. First Law of Thermodynamics 346

5. Second Law of Thermodynamics 348
   5.1. Chemical diffusion 350
   5.2. Chemical reactions and phase changes 350

6. From entropy to state and evolution laws 353
   6.1. Entropy for continuous reactive open media 353
   6.2. From entropy to behavior law – Clausius-Duhem inequality 355
   6.3. State law 358
   6.4. Evolution law 362
   6.5. Exchange laws / fluxes 365
   6.6. Heat equation and heat source expressions 366

7. Examples of multiphysical modelling in the refractory field 368
   7.1. Reactive mass transport 369
   7.2. Stress / Strain induced by mass transport 378
   7.3. Stress / Strain induced by chemical reactions and phase change 388
Chapter 7
Impact of operating conditions on refractory lining wear

1. Introduction 409

2. Adjusting the thermal gradient of the refractory lining 409
   2.1. Thermal gradient effect on refractory lining corrosion 410
   2.2. Operating conditions to form a solid slag protective layer at
       the hot face of the lining 415
   2.3. Lab experiments: formation of a solid slag crust /
       dissolution of refractory lining 421
   2.4. Discussion 429

3. Composition adjustment of the penetrant fluid 431

4. Reducing the reactivity by changing the wetting characteristics 436

5. Selecting refractory with a less porous and less permeable
   microstructure 437

6. Limit the penetration of the liquids into the refractory
   porosity by new precipitated solids that clog the pores 440
   6.1. Interaction between slag and matrix 442
   6.2. Interaction between slag and alumina aggregates 443

7. Using glazing or coating 444

8. Conclusion 446

9. References 446

Index 450