

Contents

1 Corrosion Protection Function and Breakdown Mechanism of Passive Films on Stainless Steels

Katsuhisa Sugimoto	1
1.1 Introduction	1
1.2 Origin of Pit Initiation	2
1.3 Suppression Mechanism of Passive Film Breakdown by Alloyed Cr	2
1.4 Composition of Passive Films Formed in Acid Chloride Solutions	3
1.5 Fabrication of Artificial Passivation Films	4
1.6 Evaluation of Corrosion Resistance of Artificial Passivation Films	6
1.7 Dissolution Behavior of $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ Films	7
1.8 Anodic Polarization Behavior of Fe-Cr Alloys	8
1.9 Composition of Passive Films on Fe-Cr Alloys	9
1.10 Comparison of Dissolution Behavior Between $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ Artificial Passivation Film and Real Passive Film on Fe-Cr Alloy	10
1.11 Induction Period of Pitting on Fe-Cr Alloys	11
1.12 Pitting Potentials of Fe-Cr Alloys in 1M HCl	13
1.13 Dissolution of Locally Heterogeneous $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ Film	13
1.14 Mechanism of pit Initiation on Fe-Cr Alloy	14
1.15 Summary	16
References	16

2 Passivation Oxide Films and Rust Layers on Iron

Toshiaki Ohtsuka	19
2.1 Introduction	19
2.2 Passivation Oxide Films on Iron	19
2.3 Rust Formation on Iron and Steels	26
2.4 Potential Distribution and Ionic Transport	28
2.5 Summary	30
References	31

3 Semiconductor Property of Passive Films and Corrosion Behavior of Fe-Cr Alloys

Shinji Fujimoto, Hiroaki Tsuchiya	33
3.1 Introduction	33
3.2 The Photoelectrochemical Response	33
3.2.1 A Brief History of Photoresponse in Electrochemistry	33
3.2.2 Measurement of Photocurrent and Spectrum Separation ..	34
3.3 Passive Films on Cr and Fe-Cr Alloys in Sulphuric Acid	36
3.3.1 Photocurrent	36
3.3.2 Capacitance	38
3.3.3 Electronic Structure of Passive Films on Cr and Fe-Cr Alloys formed in Acid Solution	39
3.4 Passive Film on Fe-18Cr Alloy formed in Borate Buffer Solution	42
3.4.1 Photocurrent and Capacitance	42
3.4.2 Electronic Structure of Passive Films on Fe-18Cr Alloy formed in Borate Buffer Solution	44
3.5 Correlation between Electronic Structure of Passive Films and Corrosion Behaviour for Fe-Cr Alloys	45
3.6 Summary	47
References	47

4 Mechanistic Study on Formation of Iron Hydroxides and Oxides with FT-IR and UV Photospectroscopy

Atsushi Muramatsu, Kiyoshi Kanie	51
4.1 Introduction	51
4.2 Utilization of UV-vis and FT-IR	51
4.3 Precipitation from Aqueous Solutions	54
4.4 Simplest Complex of Iron	56
4.5 Change in Ferric Complexes with pH	58
4.6 UV Spectroscopy for the Direct Identification of Ferric Complexes	59
4.7 IR Spectroscopy for the Formation Mechanism of Particles	65
4.8 Characterization of Iron Oxides by FT-IR	69
References	74

5 Structural Characterization for a Complex System by Obtaining Middle-Range Ordering

Yoshio Waseda, Shigeru Suzuki, Masatoshi Saito	77
5.1 Introduction	77
5.2 Theoretical Background and Methods	78
5.3 Selected Examples of Middle-range Ordering Obtained by the AXS Method Coupled with the RMC Simulation Technique	83
5.3.1 GeO ₂ Glass	83
5.3.2 Amorphous ZrO ₂ Prepared by Hydrolytic Condensation ..	88

5.3.3	Corrosion Products formed on the Steel Surface	93
5.4	Summary	102
	References	103
6	Corrosion Mechanism of Iron from an X-ray Structural Viewpoint	
	Eiichiro Matsubara, Shigeru Suzuki, Yoshio Waseda	105
6.1	Introduction	105
6.2	Structure and Formation of Various Components of Corrosion Products	106
6.3	Methods for In-situ and Ex-situ X-ray Diffraction	109
6.3.1	Sample Preparation	109
6.3.2	Diffraction Measurements	110
6.4	X-ray Diffraction of Corrosion Products Formed Under Various Conditions	111
6.4.1	In-situ X-ray Diffraction of Corrosion Products Formed During One-cycle Exposure to Wet and Dry Atmospheres	111
6.4.2	In-situ XRD Diffraction of Corrosion Products Formed During Multi-cycle Exposure to Wet and Dry Atmospheres	116
6.4.3	Ex-situ XRD Diffraction of Corrosion Products Extracted from Different Layers	119
6.5	Formation Conditions of Different Components of Corrosion Products	124
6.6	Summary	127
	References	128
7	Surface Analysis of Oxides and Corrosion Products Formed on Surfaces of Iron-based Alloys	
	Shigeru Suzuki	131
7.1	Introduction	131
7.2	Surface Analytical Methods	133
7.3	Characterization of Thermally Oxidized Surface Layers	135
7.3.1	Oxidation of a Compositionally Modified Surface Layer ...	136
7.3.2	Selective Oxidation of Less-noble Elements in Surface Layers	140
7.4	Iron Oxides Formed Under Atmospheric Corrosion	146
7.4.1	Fine Corrosion Products Formed on a Native Oxide Layer	147
7.4.2	Sources of Corrosion Products Formed on Iron Surfaces ...	151
7.5	Summary	155
	References	156

8 Characterization of Rust Layers on a Plain-Carbon Steel and Weathering Steels Exposed to Industrial and Coastal Atmosphere for Years

Katsuhiko Asami	159
8.1 Introduction	159
8.2 Experimental Procedures	161
8.2.1 Compositions of Steel Specimens	161
8.2.2 Exposure Conditions	163
8.2.3 Specimen Preparation for Characterization	163
8.2.4 Characterization Methods	163
8.3 Results	167
8.3.1 SEM Observation of Cross-Sections of Rust Layers	167
8.3.2 XRD Analysis of Rust Surface	168
8.3.3 EPMA Analysis of Rust Surface	170
8.3.4 EPMA Analysis of Cross-Section of Rust Layers	171
8.3.5 TEM/ED Analysis of Cross-Section of Rust Layers	177
8.3.6 In-depth Distribution of Rust Components	180
8.3.7 Abundance of Rust Components	183
8.4 Discussion	188
8.4.1 Effect of Amorphous Rust Layer	189
8.4.2 Effects of Akaganéite	192
8.4.3 Correlation between Akaganéite and Magnetite	193
8.4.4 Effect of Lepidocrocite and Goethite	194
8.4.5 α/γ^* Ratio	194
8.5 Summary	195
References	196

9 Synchrotron Radiation Study on Structure of Atmospheric Corrosion Products Formed on Steel Surfaces

Hiroyuki Konishi, Masato Yamashita, Jun'ichiro Mizuki, Hitoshi Uchida	199
9.1 Introduction	199
9.2 Composition of Protective Rust Layer Formed on Weathering Steel	200
9.3 Structural Study on the Protective Rust Layer using X-ray Absorption Spectroscopy	201
9.3.1 X-ray Absorption Fine Structure Analysis	202
9.3.2 Sample Preparation	203
9.3.3 Measurements and Results	205
9.3.4 Structural Properties of the Protective Rust Layer	212
9.4 In situ Observation of Corrosion Process in Wet/Dry Cycles	213
9.4.1 Experimental Method	213
9.4.2 Results	215
9.4.3 Discussion	219

9.5 Summary	220
References	221
 10 Analysis of Iron Rusts by X-ray Diffraction and X-ray Absorption Fine Structure Measurements	
Takenori Nakayama, Tatsuo Ishikawa	223
10.1 Introduction	223
10.2 Rust Analysis by X-ray Diffraction (XRD)	224
10.2.1 Quantitative Measurement of Rust Composition	224
10.2.2 Analysis of Crystallite Size of Rust Particle	225
10.2.3 In-situ Observation of Oxidation and Reduction Processes of Iron Rusts by Synchrotron Radiation	226
10.3 Rust Analysis by X-ray Adsorption Fine Structure (XAFS)	228
10.4 Approach of Artificial Rust Synthesis	229
10.4.1 Background of the Approach	229
10.4.2 Synthesis of Rust Particles	232
10.4.3 Particle Morphology	232
10.4.4 Specific Surface Area	234
10.4.5 XRD	234
10.4.6 Crystallite Size	236
10.4.7 Comparison of Effects of Metal Ions on Particle Size and Crystallinity of Rusts	236
10.4.8 Comprehensive Comparison of Effects of Metal Ions	239
10.4.9 Mechanism for Emergence of Corrosion Resistance	241
References	242
 11 Various Scale Analyses to Create Functioning Corrosion Products	
Masao Kimura, Tadashi Mizoguchi, Hiroshi Kihira, Michio Kaneko	245
11.1 Introduction	245
11.2 Various Scale Analyses for Structures of Corrosion Products	246
11.2.1 Ideal Structures of Iron Oxyhydroxides and Oxides	246
11.2.2 Formation Process of Corrosion Products	246
11.2.3 Surface of Corrosion Products in an Aquatic Media	250
11.3 Strategies for Preventing Corrosion	251
11.3.1 Resisting Acidification Near the Solution/Metal Interface: “ <i>pH-strategy</i> ”	251
11.3.2 Shielding the Interface against Environments: “ <i>shielding-</i> <i>strategy</i> ”	252
11.4 Analytical Techniques of Corrosion on Various Scales	252
11.4.1 In situ Observation of Reactions near the Solution/Metal Interface using Synchrotron Radiation	252

XIV Contents

11.4.2	Mössbauer Spectroscopy	254
11.5	Establishing <i>pH-strategy</i> through Analyses of Localized Corrosion on Stainless Steel	257
11.5.1	Localized Corrosion of Stainless Steel	257
11.5.2	Concentration of Metal Cations inside a Locally Corroding Part	257
11.5.3	Formation of Poly-Mo(O, OH) ₆ Octahedra	258
11.6	Establishing <i>shielding-strategy</i> through Analyses of Protective Rust on Weathering Steel	261
11.6.1	Protective Rust on Weathering Steel	261
11.6.2	Polymerization of Fe(O, OH) ₆ Octahedra through Wet and Dry Cycles	261
11.6.3	Various Scale Analyses for Structures of Protective Rust ..	262
11.7	Combination of <i>pH</i> - and <i>shielding-strategies</i> through Analyses of Protective Rust on Advanced Weathering Steel	266
11.7.1	Advanced Weathering Steel	266
11.7.2	Polymerization of (Fe, Ni)(O, OH) ₆ Octahedra through Wet and Dry Cycles	266
11.7.3	Formation of Cation-exchanging Poly-(Fe, Ni)(O, OH) ₆ ...	267
11.7.4	Various Scale Analyses of the Rust on the Advanced Weathering Steel	268
11.8	Summary	269
	References	270
 12 Mössbauer Spectroscopic Study on Rust Formed on Steel Surfaces		
	Takayuki Kamimura, Saburo Nasu	273
12.1	Introduction	273
12.2	Importance of Rust in Corrosion Process of Steel During Wet and Dry Cyclic Conditions	274
12.3	Mössbauer Spectroscopy	277
12.4	Investigation of Rust Formed on Weathering Steel and Mild Steel	282
12.5	Summary	288
	References	288
	Index	291

Characterization of Corrosion Products on Steel
Surfaces

Waseda, Y.; Suzuki, S. (Eds.)

2006, XVII, 297 p., Hardcover

ISBN: 978-3-540-35177-1