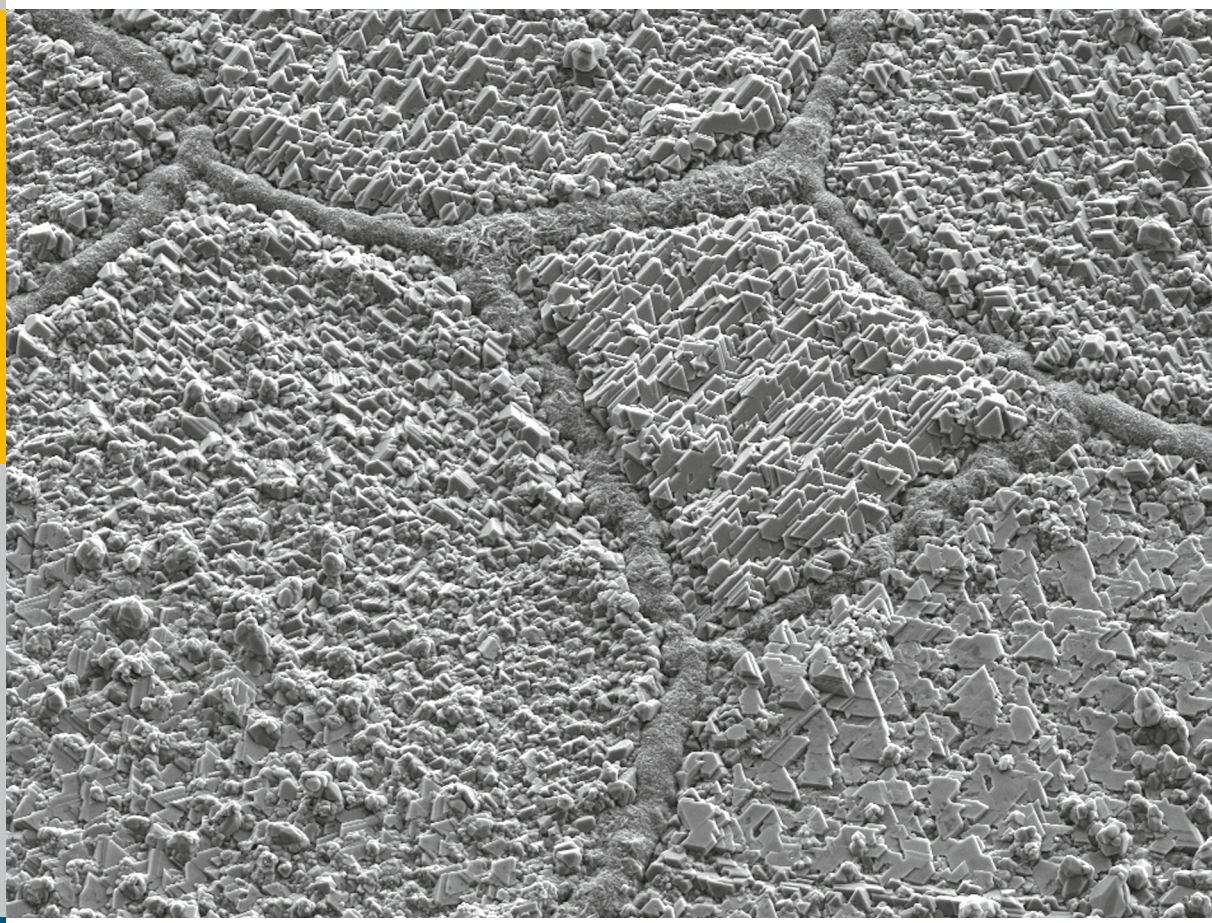
Oxidation Mechanisms of Metallic Carrier Materials for Gas Separation Membranes

Martin Schiek



Member of the Helmholtz Association

Energie & Umwelt / Energy & Environment
Band / Volume 316
ISBN 978-3-95806-138-5

JÜLICH
FORSCHUNGSZENTRUM

Forschungszentrum Jülich GmbH
Institute of Energy and Climate Research (IEK)
Microstructure and Properties of Materials (IEK-2)

Oxidation Mechanisms of Metallic Carrier Materials for Gas Separation Membranes

Martin Schiek

Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment Band / Volume 316

ISSN 1866-1793 ISBN 978-3-95806-138-5

Index

1 Introduction 1

2 Fundamentals of Alumina-forming NiCrAl-base Alloys 6

3 Aims of the Studies 8

4 Theory of High Temperature Corrosion 9

4.1 Thermodynamics 9

4.1.1 Fundamentals 9

4.1.2 Dissociation Pressure 10

4.1.3 Oxidation in H_2O/H_2 and CO_2/CO Mixtures 12

4.1.4 Ellingham Diagram 14

4.2 Oxidation Kinetics 15

4.2.1 Oxide Growth 15

4.2.2 Correlation between Oxide Thickness and Weight Change 17

4.3 Oxidation of Alloys 18

4.3.1 Transient Oxidation Stage 19

4.3.2 Internal Oxidation 21

4.3.2.1 Internal Oxidation in the Absence of an External Oxide Scale 21

4.3.2.2 Internal Oxidation in the Presence of an External Oxide Scale 27

4.3.3 Transition from Internal to External Oxidation 29

4.3.4 Maintenance of External Oxide Scale Growth 31

5 Experimental 33

5.1 Studied Materials 33

5.2 Sample Preparation 34

5.3 Oxidation Experiments 34

5.4 Test Parameters 35

5.5 Sample Characterization 36

5.5.1 SEM/EDX 37

5.5.2 XRD ... 37
5.5.3 GD-OES ... 38
5.5.4 SNMS ... 39
5.5.5 Fluorescence Spectroscopy ... 39
6 Results and Discussion ... 40
6.1 Oxidation Behavior of Alloy 602 CA ... 40
6.1.1 Phase Composition and Microstructure of Alloy 602 CA ... 40
6.1.2 Results of the Behavior in Ar-20%O_2 and H_2O-Containing Gases ... 41
6.1.2.1 Oxidation Kinetics ... 41
6.1.2.2 Oxide Scale Formation ... 43
6.1.2.3 Internal Oxidation and Carbide Depleted Zones ... 56
6.1.3 Discussion of the Behavior in Ar-20%O_2 and H_2O-Containing Gases ... 58
6.1.3.1 External Chromia Scale Formation in Different Environments ... 58
6.1.3.2 Incorporation of Titanium into Chromia Scales ... 60
6.1.3.3 External Alumina Scale Formation ... 60
6.2 Oxidation Behavior of Haynes 214 ... 71
6.2.1 Phase Composition and Microstructure of Haynes 214 ... 71
6.2.2 Oxidation Behavior in Ar-20%O_2 ... 74
6.2.2.1 Oxidation Kinetics ... 74
6.2.2.2 Oxide Scale Formation ... 77
6.2.2.3 Formation of Precipitate Free Zone (PFZ) ... 83
6.2.3 Discussion of the Oxidation Behavior in Ar-20%O_2 ... 87
6.2.3.1 Time and Temperature Dependence of the Oxide Scale Morphology ... 87
6.2.3.2 Effect of γ′-Precipitation on Oxidation Behavior ... 90
6.2.3.3 Effect of Aging Treatments on Oxidation Behavior ... 92
6.2.3.3.1 Oxidation Kinetics of Aged Haynes 214 ... 92
6.2.3.3.2 Oxide Scale Morphology ... 94

6.2.3.4 Proposed Oxidation Mechanisms 96
6.2.4 Behavior of Haynes 214 in H_2O-Containing Gases Compared with Ar-20%O_2 103
6.2.4.1 Behavior in Ar-7%H_2O 103
6.2.4.2 Behavior in Ar-4%H_2-7%H_2O 107
6.2.4.3 Behavior in Ar-20%O_2-7%H_2O 112
6.2.5 Discussion of the Behavior in H_2O-containing Gases Compared to Ar-20%O_2. 117
7 Effects of Alloy Composition Variation 121
8 Considerations Related to Material Geometry and Oxidation Behavior 126
9 Summary and Conclusion 129
10 References 133
Appendix A – Buoyancy Effect 145
Appendix B – Instantaneous Oxidation Rate Constant 147

Energie & Umwelt /
Energy & Environment
Band / Volume 316
ISBN 978-3-95806-138-5