

## Forschungsberichte

Nr. 17

Weilin Wang

2019

Corrosion mechanisms and models for flue gas corrosion in aluminium heat exchangers

“Corrosion mechanisms and models for flue gas corrosion in aluminium heat exchangers”

Von der Fakultät für Georessourcen und Materialtechnik  
der Rheinisch-Westfälischen Technischen Hochschule Aachen

Zur Erlangung des akademischen Grades eines

Doktors der Ingenieurwissenschaften

genehmigte Dissertation

vorgelegt von **M.Sc.**

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Tag der mündlichen Prüfung: 19. Februar 2019



Schriftenreihe des DECHEMA-Forschungsinstituts

Band 17

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**Corrosion mechanisms and models for flue  
gas corrosion in aluminium heat exchangers**

Shaker Verlag  
Aachen 2019

**Bibliographic information published by the Deutsche Nationalbibliothek**

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

Zugl.: D 82 (Diss. RWTH Aachen University, 2018)

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Printed in Germany.

ISBN 978-3-8440-6589-3

ISSN 2197-6155

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen

Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9

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## Acknowledgments

This research project is supported by Dechema Research Institute, Bosch Thermotechnology (part of Robert Bosch GmbH group) and Materials innovation institute (M2i). I would like to thank for giving me this wonderful opportunity and for their financial support.

First and foremost I would like to thank my daily supervisor PD Dr.-Ing. W. Fürbeth, who gave me the opportunity to do this project, who shared his knowledge and experience with me, who provided me the guidance and endless support I needed to get through the difficulties.

I would also like to thank the cluster leader Prof. Herman Terryn from m2i, who provided valuable suggestions in completion of this research project, as well as the program manager Bert van Haastrecht for his constant support.

Special thanks are directed to Dr. Alessandro Pecenko, Dr. Wolf Schmid and Mr. Gert-Jan Feberwee, my excellent industrial supervisors from Bosch Thermotechnology (Research & Development) for introducing me to the world of condensing boiler and for their great collaboration, support and guidance through the course of this project.

To my colleagues in Dechema Research Institute: Antonio, thanks for patience guidance and valuable help with all the design and assembly of test instruments in the lab. Daria, thank you for all your selfless help during these years, especially with OCP and EIS measurements. Sigrid, Britta and David, thank you for the help and care in the work. Dr. Klaus-Michael, thanks for the professional discussion with EIS and for your lab safety work. I am also grateful to Dr. Depentori and Dr. Kuznetsov for their support with AFM and SKPFM. To Serkan and Jürgen for their help in the lab. To Dr. Sakthivel for the introduction of Raman Spectroscopy. To Dr. Schmidt for his very kind help with EPMA and XPS. In addition, special thanks to Ellen, Daniela, Susan and Melanie for their support with SEM/EDX and sample preparation.

Lastly, special thanks go to my parent who always support and encourage me. To my husband for your constant encouragement and belief in me and for teaching me so many things about life. To my lovely son, Frank, who is my biggest source of strength during my study.

## Abstract

In the recent years condensing wall-hung gas-fired boilers have become the benchmark product in their class of appliances for residential heating with fossil fuels. Much of their success is due to their high efficiency, which exceeds 100% thanks to the contribution from the condensation latent heat of the water vapor contained in the flue gas (also known as “dew point condensation”). However, the overall size of the appliance has received the attention of the engineers as well, to respond to the increasing lack of space in newly built city apartments. In this regard, finned heat exchangers are among the most suitable configurations, and are considered as reference design in the present research work. Due to the compact construction of the heat exchanger, its narrow gas channels are easily clogged by corrosion products which represent an unavoidable side-effect of dew point corrosion. As a result, the clogged heat exchanger can give rise to malfunctioning of the condensing boiler, which should be avoided. In addition, because of an increasing number of condensing boilers which are produced every year, there is a great interest in having a model that can predict dew point corrosion. However, a lack of knowledge about corrosion mechanisms and corrosion rates has become a limiting factor in the development of such a model. Therefore it is important to obtain a deep understanding of the dew point corrosion behavior of heat exchangers.

The additional heat from the flue gas is being reused by the condensing boiler, as it flows through the heat exchanger. Condensation of combustion products ( $H_2O$ ,  $CO_2$ ,  $SO_x$ ,  $NO_x$ , HCl) from natural gas occurs where the temperature locally drops below the dew point of the gas mixture, which yields a film of acidic solution ( $H_2SO_4$ , HCl,  $HNO_3$ ,  $H_2O$ ) on each surface of the boiler heat exchanger that is exposed to the flue gas flow during the boiler’s burning cycles. The concentration of this acidic condensate changes according to the temperature gradient along the heat exchanger, which leads to various corrosion mechanisms. Since the condensation of sulfuric acid is the biggest problem as compared to other acids, the experiments conducted in this work involve sulfuric acid of various concentrations. The final target of the experimental investigation was the determination of the main parameters affecting the dew point corrosion rates on the heat exchanger fins.

Before the corrosion tests, it has been necessary to have a deeper look at the microstructure of the heat exchanger material (AlSi12(Fe)), which is mainly determined by the composition of the alloying elements. The intermetallic phases (IMPs) formed from the alloying elements lead to a higher susceptibility to localized corrosion, like pitting, intergranular and exfoliation corrosion. Combining immersion tests and electrochemical measurements, a detailed characterization of IMPs in AlSi12(Fe) alloys is conducted, and their influence on the corrosion behavior in diluted and concentrated sulfuric acid solutions is studied. In addition, the influence of the pH value and the temperature on the corrosion products and mechanisms are discussed for a full understanding of the corrosion behaviours in sulfuric acid medium.

A dew point corrosion setup has been developed to simulate the real conditions in the flue gas. In order to understand the dew point corrosion behavior, the factors that influence the acid condensation rate and corrosion rate according to the temperature gradient are focused on. In contrast to immersion tests, the influence of acid condensation and the build-up of a protective layer of corrosion products can be taken into account in the dew point corrosion tests. It can be concluded that the dew point corrosion rate is mainly affected by the acid condensation rate, the acid temperature and the characteristic features of the material.

## Kurzfassung

In den nächsten Jahren sollen neuartige Brennwertkessel mit kompakteren und effizienteren Wärmetauschern auf den Markt kommen. Aufgrund des geringeren spezifischen Gewichts und geringerer Kosten wird der neue Wärmetauscher aus einer AlSi-Legierung und nicht aus Stahl hergestellt. Die kompakte Bauweise der Wärmetauscher mit sehr schmalen Gaskanälen führt zu einer schnellen Verblockung dieser Kanäle durch Korrosionsprodukte, welche durch Taupunktkorrosion entstehen. Der verstopfte Wärmetauscher führt schließlich zum Ausfall des Brennwertkessels, was vermieden werden sollte. Da die Zahl der produzierten Brennwertkessel von Jahr zu Jahr steigt, besteht ein großes Interesse daran, ein Modell zu haben, welches die Taupunktkorrosion vorhersagen kann. Bisher ist das fehlende Wissen über die zugrundeliegenden Korrosionsmechanismen und Korrosionsraten der limitierende Faktor für die Entwicklung eines solchen Modells. Daher ist es wichtig, ein tieferes Verständnis über die Taupunktkorrosion von Wärmetauschern zu erzielen.

Um den thermischen Wirkungsgrad des Kessels zu erhöhen, wird die zusätzliche Wärme der Abgase genutzt, wenn sie den Wärmetauscher durchlaufen. Dabei bilden sich an den Stellen, an denen die Temperatur unter die Taupunkttemperatur der Gasmischung sinkt, Kondensate der Verbrennungsprodukte ( $H_2O$ ,  $CO_2$ ,  $SO_x$ ,  $NO_x$ ,  $HCl$ ) des Erdgases. Diese Kondensate bilden saure Lösungen ( $H_2SO_4$ ,  $HCl$ ,  $HNO_3$ ,  $H_2O$ ). Die Konzentration der sauren Kondensate ändert sich in Abhängigkeit des Temperaturgradienten innerhalb des Wärmetauschers, was zu unterschiedlichen Korrosionsmechanismen führen kann. Da die Kondensation von Schwefelsäure, verglichen mit den anderen Säuren, das größte Problem darstellt, beschäftigen sich die Experimente in dieser Arbeit mit dem Einfluss von Schwefelsäure in unterschiedlichen Konzentrationen.

Vor den Korrosionsuntersuchungen wird zunächst die Mikrostruktur des Wärmetauschermaterials (AlSi12(Fe)), welche vornehmlich durch die Zusammensetzung der Legierungselemente bestimmt wird, genauer untersucht. Intermetallische Phasen (IMPs), die durch die Legierungselemente gebildet werden, führen zu einer erhöhten Anfälligkeit für lokale Korrosion, wie Loch-, interkristalline oder Schichtkorrosion. Mithilfe der Kombination von Immersionstests und elektrochemischen Korrosionsuntersuchungen

wird eine detaillierte Charakterisierung der IMPs in der AlSi12(Fe)-Legierung durchgeführt und deren Einfluss auf das Korrosionsverhalten in verdünnter und konzentrierter Schwefelsäure untersucht. Zusätzlich wird der Einfluss des pH-Wertes und der Temperatur auf die Korrosionsprodukte und Korrosionsmechanismen diskutiert, um das Korrosionsverhalten in Schwefelsäure vollständig zu beschreiben.

Es wurde eine Versuchsanlage zur Simulation der Taupunktkorrosion entwickelt. Um das Taupunktkorrosionsverhalten des Werkstoffes aufzuklären, standen der Einfluss der Säurekondensationsrate und der Korrosionsrate in Abhängigkeit des Temperaturgradienten im Mittelpunkt der Untersuchungen. Im Gegensatz zu den Immersionstests müssen bei den Taupunktkorrosionsversuchen der Einfluss der Säurekondensation und die Ausbildung einer schützenden Deckschicht aus Korrosionsprodukten in Betracht gezogen werden. Aus den Untersuchungen wird geschlossen, dass die Taupunktkorrosionsrate hauptsächlich durch die Säurekondensationsrate, die Säuretemperatur und die Charakteristik des Werkstoffs bestimmt wird.

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## Table of Contents

<b>1</b>	<i>Introduction</i> .....	<b>1</b>
<b>1.1</b>	Background .....	1
<b>1.2</b>	Outline of the thesis .....	3
<b>2</b>	<i>Literature review</i> .....	<b>6</b>
<b>2.1</b>	Aluminium and aluminium alloys .....	6
2.1.1	Aluminium casting alloys.....	6
2.1.2	Aluminium-silicon die casting alloys .....	7
2.1.3	Iron containing aluminium-silicon alloys.....	10
<b>2.2</b>	Corrosion behaviour of aluminium and aluminium alloys .....	12
2.2.1	Stability of aluminium oxide film .....	13
2.2.2	Corrosion of aluminium alloys.....	14
2.2.3	Corrosion of aluminium-silicon alloys.....	16
2.2.4	Corrosion products of aluminium .....	18
<b>2.3</b>	Types of corrosion.....	19
2.3.1	Uniform corrosion.....	19
2.3.2	Transgranular and intergranular corrosion .....	20
2.3.3	Exfoliation corrosion.....	20
2.3.4	Pitting corrosion.....	20
2.3.5	The role of intermetallic phases in localized corrosion of aluminium alloys .....	25
<b>2.4</b>	Electrochemical investigations on aluminium and aluminium alloys .....	26
2.4.1	Open circuit potential.....	26
2.4.2	Electrochemical impedance spectroscopy (EIS) .....	27
<b>2.5</b>	Dew point corrosion .....	30
2.5.1	Flue gas dew point corrosion in condensing boilers .....	30
2.5.2	Recent research specific to acid dew point corrosion .....	32
2.5.3	Condensation and condensation rate under dewing conditions .....	34
2.5.4	Influencing factors on the dew point corrosion rate .....	41
2.5.5	Investigation methods in dew point corrosion.....	43

<b>3</b>	<b><i>Experimental setup and procedure</i></b>	<b>46</b>
<b>3.1</b>	<b>Materials and samples preparation</b>	<b>46</b>
<b>3.2</b>	<b>Corrosion tests</b>	<b>47</b>
3.2.1	Immersion tests .....	47
3.2.2	Electrochemical Tests.....	49
3.2.3	Dew point corrosion tests .....	50
<b>3.3</b>	<b>Characterization techniques</b>	<b>55</b>
3.3.1	Scanning Electron Microscopy (SEM) with X-ray Energy Dispersive Spectroscopy (EDS).55	
3.3.2	Electron probe micro-analysis (EPMA) by X-ray wavelength dispersive spectroscopy.... 56	
3.3.3	Atomic force microscopy (AFM) and scanning Kelvin probe force microscopy (SKPFM) .56	
3.3.4	Raman microprobe spectroscopy .....	57
<b>4</b>	<b><i>Characterization of the material</i></b>	<b>58</b>
<b>4.1</b>	<b>Identification of intermetallic phases by SEM and EPMA</b>	<b>58</b>
<b>4.2</b>	<b>Microstructure analysis by AFM and SKPFM.....</b>	<b>60</b>
<b>5</b>	<b><i>Immersion corrosion tests</i></b>	<b>63</b>
<b>5.1</b>	<b>Immersion tests in diluted sulfuric acid solution</b>	<b>63</b>
5.1.1	1% sulfuric acid immersion tests .....	66
5.1.2	0.1% sulfuric acid immersion tests .....	69
<b>5.2</b>	<b>Immersion tests in concentrated sulfuric acid solution</b>	<b>72</b>
<b>5.3</b>	<b>Mechanistic investigation of corrosion initiation in sulfuric acid.....</b>	<b>76</b>
5.3.1	The role of IMPs in the initial stage of corrosion .....	76
5.3.2	The dissolution of IMPs .....	82
<b>5.4</b>	<b>Mechanistic investigations of corrosion propagation in sulfuric acid .....</b>	<b>83</b>
5.4.1	Corrosion propagation in diluted sulfuric acid .....	83
5.4.2	Corrosion propagation in concentrated sulfuric acid .....	87
<b>5.5</b>	<b>Characterization of the corrosion products .....</b>	<b>89</b>
5.5.1	The white precipitates in diluted sulfuric acid.....	89
5.5.2	Characterization of white corrosion products in concentrated sulfuric acid .....	94
<b>5.6</b>	<b>Immersion tests in neutral solution .....</b>	<b>95</b>
<b>5.7</b>	<b>Summary of immersion corrosion tests and mechanistic investigations .....</b>	<b>98</b>

<b>6    <i>Electrochemical investigations on the corrosion mechanism in diluted sulfuric acid and neutral solution</i></b> .....	<b>103</b>
<b>6.1    OCP measurements in diluted sulfuric acid</b> .....	<b>103</b>
<b>6.2    Combining OCP and pH measurement to find the critical value</b> .....	<b>114</b>
<b>6.3    EIS measurements in diluted sulfuric acid</b> .....	<b>116</b>
6.3.1    Nyquist plots.....	116
6.3.2    Model description.....	120
<b>6.4    EIS measurements in neutral solution</b> .....	<b>126</b>
<b>6.5    EIS measurement of pure AlSi12 alloy in neutral solution</b> .....	<b>132</b>
<b>6.6    Summary</b> .....	<b>133</b>
<b>7    <i>Dew point corrosion tests</i></b> .....	<b>136</b>
<b>7.1    Investigations on the condensation rate in acid dew point tests</b> .....	<b>136</b>
7.1.1    Influence of the temperature of the gas phase on the condensation rate .....	140
7.1.2    Influence of the gas flow rate on the condensation rate .....	141
7.1.3    Influence of the sulfuric acid concentration on the condensation rate .....	142
<b>7.2    Investigations on the condensation rate in water dew point tests</b> .....	<b>143</b>
<b>7.3    Investigations on the dew point corrosion rate</b> .....	<b>145</b>
7.3.1    Influence of the condensation rate on the corrosion rate .....	149
7.3.2    Influence of the corrosion products on the corrosion rate .....	151
7.3.3    Influence of the local temperature on the corrosion rate .....	151
7.3.4    Influence of the acid concentration on the corrosion rate .....	151
<b>7.4    Summary</b> .....	<b>152</b>
<b>8    <i>Conclusions and suggestions for future work</i></b> .....	<b>155</b>
<b>References</b> .....	<b>159</b>