Edited by Michael Schütze,
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WILEY-VCH

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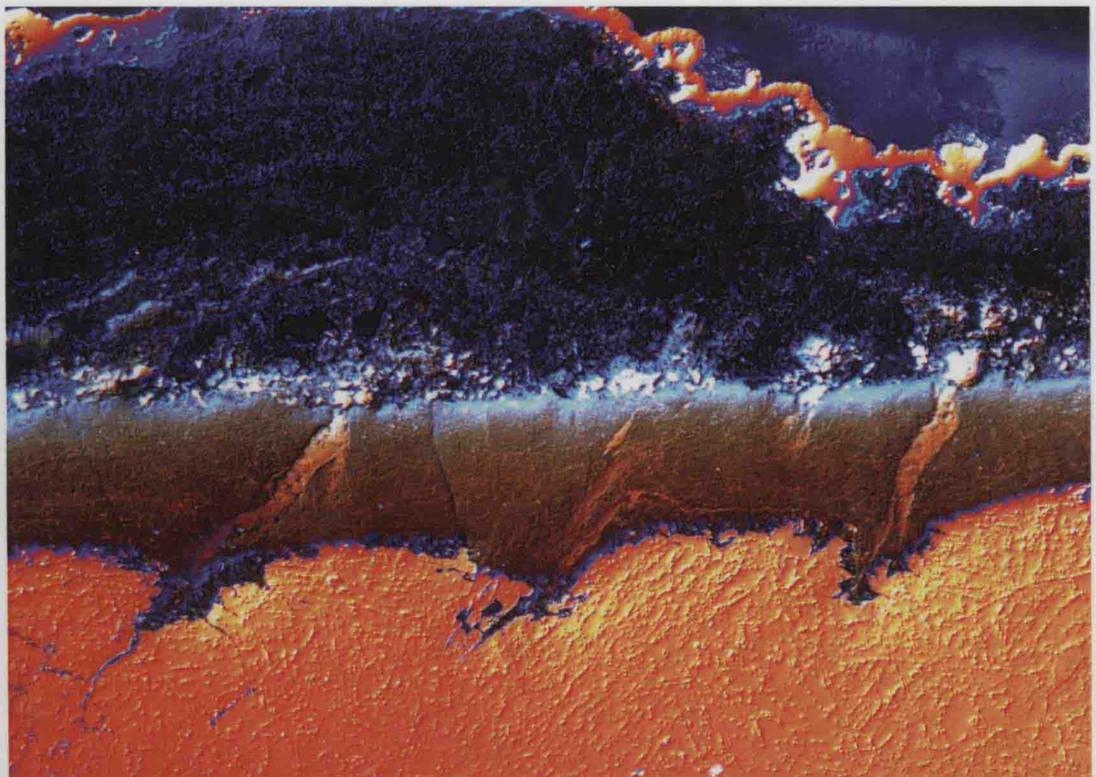

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Corrosion Resistance of Nickel and Nickel Alloys Against Acids and Lyes

DECHEMA

WILEY-VCH
Verlag GmbH & Co. KGaA

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Cover Illustration
Source: DECHEMA-Forschungsinstitut,
Frankfurt (Main), Germany

Library of Congress Card No.: Applied for.

British Library Cataloguing-in-Publication Data:
A catalogue record for this book is available from the British Library.

Bibliographic information published by Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <http://dnb.ddb.de>.

Printed in the Federal Republic of Germany
Printed on acid-free paper

Typesetting Kühn & Weyh, Satz und Medien, Freiburg
Printing Strauss GmbH, Mörlenbach
Binding Strauss GmbH, Mörlenbach
Cover Design Graphik-Design Schulz, Fußgönheim

ISBN: 978-3-527-33849-8

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Preface

Practically all industries face the problem of corrosion – from the micro-scale of components for the electronics industries to the macro-scale of those for the chemical and construction industries. This explains why the overall costs of corrosion still amount to about 2 to 4% of the gross national product of industrialized countries despite the fact that billions of dollars have been spent on corrosion research during the last few decades.

Much of this research was necessary due to the development of new technologies, materials and products, but it is no secret that a considerable number of failures in technology nowadays could, to a significant extent, be avoided if existing knowledge were used properly. This fact is particularly true in the field of corrosion and corrosion protection. Here, a wealth of information exists, but unfortunately in most cases it is scattered over many different information sources. However, as far back as 1953, an initiative was launched in Germany to compile an information system from the existing knowledge of corrosion and to complement this information with commentaries and interpretations by corrosion experts. The information system, entitled "DECHEMA-WERKSTOFF-TABELLE" (DECHEMA Corrosion Data Sheets), grew rapidly in size and content during the following years and soon became an indispensable tool for all engineers and scientists dealing with corrosion problems. This tool is still a living system today: it is continuously revised and updated by corrosion experts and thus represents a unique source of information. Currently, it comprises more than 12,000 pages with approximately 110,000 corrosion systems (i.e., all relevant commercial materials and media), based on the evaluation of over 100,000 scientific and technical articles which are referenced in the database.

Last century, an increasing demand for an English version of the DECHEMA-WERKSTOFF-TABELLE arose in the 80's; accordingly the first volume of the DECHEMA Corrosion Handbook was published in 1987. This was a slightly condensed version of the German edition and comprised 12 volumes. Before long, this handbook had spread all over the world and become a standard tool in countless laboratories outside Germany. The second edition of the DECHEMA Corrosion Handbook was published in 2004. Together the two editions covered 24 volumes.

The present handbook compiles new and updated information on the corrosion behavior of nickel and nickel alloys in contact with the following aggressive media: acetic acid, alkanecarboxylic acids, carbonic acid, fluorine and hydrofluoric acid, formic acid, hydrochloric acid, mixed acids, nitric acid, phosphoric acid, sulfonic acids, sulfuric acid, alkaline earth hydroxides, lithium hydroxide, potassium hydroxide and sodium hydroxide.

Nickel and nickel-base alloys are vitally important to modern industry due to their ability to withstand a wide variety of severe operating conditions involving corrosive environments, high temperatures, high stresses, and combinations of these factors.

Nickel and its alloys range in composition from commercially pure nickel to complex alloys containing many alloying elements, and like the stainless steels, offer a wide range of corrosion resistance. However, nickel can accommodate larger amounts of alloying elements – mainly chromium, molybdenum, and tungsten – in solid solution than iron. Therefore, nickel-base alloys in general can be used in more severe environments than the stainless steels.

Nickel-base alloys are used for corrosion resistance or for combined corrosion resistance and high temperature strength in a wide range of commercial applications. These various applications may demand resistance to aqueous corrosion mechanisms, such as general corrosion, localized attack, and stress corrosion cracking.

Understanding how to improve the corrosion resistance of nickel and nickel alloys used as reaction, transport and storage vessels against these omnipresent chemicals is crucial for all industries involved. This book is therefore an indispensable tool for all mechanical, civil and chemical engineers, material scientists and chemists working with nickel and nickel alloys in alkaline or acidic media.

This handbook highlights the limitations of nickel and nickel alloys in acids and lyes and provides vital information on corrosion protection measures. The chapters are arranged by the media leading to individual corrosion reactions, and a vast number of alloys are presented in terms of their behavior in these media. The key information consists of quantitative data on corrosion rates coupled with commentaries on the background and mechanisms of corrosion behind these data, together with the dependencies on secondary parameters, such as flow-rate, pH, temperature, etc. This information is complemented by more detailed annotations where necessary, and by an immense number of references listed at the end of each chapter.

An important feature of this handbook is that the data was compiled for industrial use. Therefore, particularly for those working in industrial laboratories or for industrial clients, the book will be an invaluable source of rapid information for day-today problem solving. The handbook will have fulfilled its task if it helps to avoid the failures and problems caused by corrosion simply by providing a comprehensive source of information summarizing the present state-of-the-art. Last but not least, in cases where this knowledge is applied, there is a good chance of decreasing the costs of corrosion significantly.

Finally the editors would like to express their appreciation to Dr. Rick Durham and Dr. Horst Massong for their admirable commitment and meticulous editing of a work that is encyclopedic in scope.

Michael Schütze, Raul B. Rebak and Roman Bender

How to use the Handbook

The Handbook provides information on the chemical resistance and the corrosion behavior of nickel and nickel alloys in acids and lyes.

The user is given information on the range of applications and corrosion protection measures.

Research results and operating experience reported by experts allow recommendations to be made for the selection of materials and to provide assistance in the assessment of damage.

The objective is to offer a comprehensive and concise description of the behavior of nickel in contact with a particular medium.

The information on resistance is given as text, tables, and figures. The literature used by the authors is cited at the corresponding point. There is an index of materials as well as a subject index at the end of the book so that the user can quickly find the information given for a particular keyword.

The Handbook is thus a guide that leads the reader to nickel and nickel alloys that have already been used in certain cases, that can be used or that are not suitable owing to their lack of resistance.

The resistance is labeled with three evaluation symbols in view of concise presentation. Uniform corrosion is evaluated according to the following criteria:

Symbol	***Meaning***	***Area-related mass loss rate*** x		***Corrosion rate*** y
		g/m^2 h	g/m^2 d	mm/a
+	resistant	≤ 0.1	≤ 2.4	≤ 0.1
⊕	moderately resistant	> 0.1 to ≤ 1.0	> 2.4 to ≤ 24.0	> 0.1 to ≤ 1.0
–	not resistant	> 1.0	> 24.0	> 1.0

The evaluation of the corrosion resistance of metallic materials is given

- for uniform corrosion or local penetration rate, in: mm/a and mpy
- or if the density of the material is not known, in: g/m^2 h or g/m^2 d.

Pitting corrosion, crevice corrosion, and stress corrosion cracking or non-uniform attack are particularly highlighted.

The following equations are used to convert mass loss rates, x, into the corrosion rate, y:

from x_1 in g/m^2 h

$$\frac{x_1 \cdot 365 \cdot 24}{\rho \cdot 1{,}000} = y\ (mm/a)$$

from x_2 in g/m^2 d

$$\frac{x_2 \cdot 365}{\rho \cdot 1{,}000} = y\ (mm/a)$$

where

x_1: value in g/m^2 h
y: value in mm/a
x_2: value in g/m^2 d
d: days
ρ: density of material in g/cm^3
h: hours

In those media in which uniform corrosion can be expected, if possible, isocorrosion curves (corrosion rate y = 0.1 mm/a) are given.

Unless stated otherwise, the data was measured at atmospheric pressure and room temperature.

The resistance data should not be accepted by the user without question, and the materials for a particular purpose should not be regarded as the only ones that are suitable. To avoid wrong conclusions being drawn, it must be always taken into account that the expected material behavior depends on a variety of factors that are often difficult to recognize individually and which may not have been taken deliberately into account in the investigations upon which the data is based. Under certain circumstances, even slight deviations in the chemical composition of the medium, in the pressure, in the temperature or, for example, in the flow rate are sufficient to have a significant effect on the behavior of the materials. Furthermore, impurities in the medium or mixed media can result in a considerable increase in corrosion.

The composition or the pretreatment of the material itself can also be of decisive importance for its behavior. In this respect, welding should be mentioned. The suitability of the component's design with respect to corrosion is a further point which must be taken into account. In case of doubt, the corrosion resistance should be investigated under operating conditions to decide on the suitability of the selected materials.

Contents

Warranty disclaimer

This book has been compiled from literature data with the greatest possible care and attention. The statements made in this book only provide general descriptions and information.

Even for the correct selection of materials and correct processing, corrosive attack cannot be excluded in a corrosion system as it may be caused by previously unknown critical conditions and influencing factors or subsequently modified operating conditions.

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Acetic Acid

Author: *G. Elsner* / Editor: *R. Bender, R. Durham*

Nickel

– Acetic acid –

Boilers made from nickel or NiCu-alloys have proven to be suitable for the hydrogenation (even under pressure) of substances dissolved in glacial acetic acid [1, 2].

The electrochemical behavior of nickel in acetic acid solutions was investigated in [3].

However, the corrosion resistance of nickel in acetic acid depends greatly on the presence of air, oxygen and other oxidizing agents; see Table 1.

Metal	*Acetic acid %*	*Temperature °C*	*Corrosion rate mm/a*	*Remarks*	*Literature*
Nickel	50	20	< 0.1		[4]
	50	100	< 3.0		
	conc.*	20	< 0.1		
	conc.	100	< 10.0		
	1–100	20	0.04–0.202	air free	[2]
	1–100	boiling	0.202–0.607	slightly aerated	
	1–100	20	0.202–0.607	moderately aerated	
	1–100	20	1.01–1.62	vigorously aerated, stirred	
	6	30	0.001–0.01	not aerated	[5]
	10	boiling	1.01–3.03		
	50	boiling	0.101–1.01		
	6	30	0.101–1.01	aerated	[5]
	10	30	1.01–3.03	aerated	
	95	115	> 10.1	aerated, technical grade acetic acid, 95%	
	5	boiling	0.267	liquid phase	[1, 2, 4]
	5	boiling	0.186	vapor phase	

* concentrated

Table 1: Corrosion behavior of nickel in acetic acid of various concentrations and temperatures

Table 1: Continued

Metal	*Acetic acid %*	*Temperature °C*	*Corrosion rate mm/a*	*Remarks*	*Literature*
Nickel	50	boiling	0.485	liquid phase	
	50	boiling	0.364	vapor phase	
	98	boiling	0.299	liquid phase	
	98	boiling	0.097	vapor phase	
	99.9	boiling	0.344	liquid phase	
	99.9	boiling	0.057	vapor phase	
	6	20	0.05	6% acetic acid + hydrogen	[4]
	50	50	0.25	50% acetic acid + hydrogen	
	100	20	0.10	100% acetic acid + hydrogen	
	99.5	112.2	0.1325	99.5% acetic acid + 0.05% salicylic acid + 0.45% water, vapor/ 1,022 h, operational test	[1, 6]
Nickel, 99%	10–100	24	> 1.25	aerated	[7]
	10–20	24	< 0.05	air-free	[7, 8]
	30	24	0.5–1.25		
	40–100	24	< 0.5		
	50	52	0.5–1.25		
	90–100	100	< 0.5		
	100	100	< 0.5	acetic acid vapor, air-free	[7]
	100	100	0.5–1.25	acetic acid + acetic anhydride + peracetic acid	[7, 8]
	100	24	> 1.25	acetic acid + hydro-bromic acid	[7, 8]

* concentrated

Table 1: Corrosion behavior of nickel in acetic acid of various concentrations and temperatures

Table 1: Continued

Metal	*Acetic acid %*	*Temperature °C*	*Corrosion rate mm/a*	*Remarks*	*Literature*
Nickel, 99%	100	24	> 1.25	acetic acid + hydrochloric acid	[7, 8]
	100	100	< 0.5	acetic acid + salicylic acid vapors	[7, 8]
	100	100	0.5–1.25	acetic acid + cupric acetate + chlorides	[8]

* concentrated

Table 1: Corrosion behavior of nickel in acetic acid of various concentrations and temperatures

Anhydrous acetic acid dissolved in organic solvents, for example benzene, is virtually non-aggressive towards nickel [1, 9].

In contrast to the stainless steels, nickel and Monel® are more resistant to acetic acid/formic acid mixtures than to glacial acetic acid, in particular in the presence of more than 2% formic acid at temperatures of more than 120°C [10].

NiP-coatings deposited at zero current containing 14% phosphorus and having a layer thickness of 0.025 to 0.035 mm are attacked by glacial acetic acid even at room temperature. Heat treatment (1 h at 400°C) slightly improves the corrosion resistance [11].

Ni-coatings deposited at zero current are severely attacked, amongst others, by 5% acetic acid [12].

Ni-coatings (about 0.076 mm thick) produced at zero current by the Kanigen process have corrosion rates listed in Table 2 after a heat treatment at 760°C.

Acetic acid concentration, %	*Corrosion rate, mm/a*
5	0.0033 (0.13)*
10	0.0017
50	0.0020
Glacial acetic acid	0.00025

* value for the non-heat treated material

Table 2: Corrosion rates of Ni-coatings (heat-treated) in acetic acid of various concentrations [13]

The self-fluxing Ni-hard alloy PG-Sr3 deposited on the steel 12Ch18N10T was investigated for its corrosion and wear resistance in acetic acid. The material consumption rate of the coating was determined to be 0.003 to 0.005 g/m^2 h. A coating formed in 10 s at 917°C at 52 MPa under friction in acetic acid showed the best wear resistance [14].

According to a patent, Ni-coatings on stainless hardened nitrated or galvanized steels can be removed by anodization in solutions with ammonium nitrate, ammonium chloride and acetic acid without corrosion of the steels [15]. Cast nickel ((%) Ni-1.6Si-0.5C) and Duranickel® 301 ((%) Ni-0.05Cu-0.15Fe-0.55Si-0.25Mn-0.15C-4.5Al-0.5Ti) [1, 16] show the same corrosion behavior in acetic acid as pure nickel (Nickel® 200 (%) Ni-0.05Cu-0.15Fe-0.05Si-0.25Mn-0.06C and Nickel® 201 (%) Ni-0.05Cu-0.15Fe-0.05Si-0.20Mn-0.01C) [16, 17].

The acetic salt spray, the Corrodcote or the Kesternich test are used as accelerated test methods for the evaluation of the usability of NiP-coatings for the oil and gas industry [5].

According to numerous tables, the addition of mercury sulfate is said to decrease the corrosion of nickel; however, these data should be examined [2].

– Acetic acid vapor –

Above 300°C, acetic acid vapors are more or less extensively catalytically decomposed at the surface of nickel and its alloys [1, 2].

– Acetic anhydride –

If air is excluded, nickel and NiCu-alloys are resistant to acetic anhydride containing up to 5% acetic acid up to the boiling point [18].

As for the corrosion behavior of nickel in acetic anhydride see Table 3.

– Acetic anhydride vapor –

At temperatures above 400°C, acetic anhydride vapors are decomposed catalytically on nickel and its alloys [18].

– Vinegar –

Food products do not or only slightly attack nickel. Traces of nickel which are absorbed by certain food products are not harmful to health [19].

Nickel-chromium alloys

– Acetic acid –

For the corrosion behavior of NiCr-alloys [20] in acetic acid, see Table 4.