Edited by Michael Schütze,
Günter Schmitt, and Roman Bender

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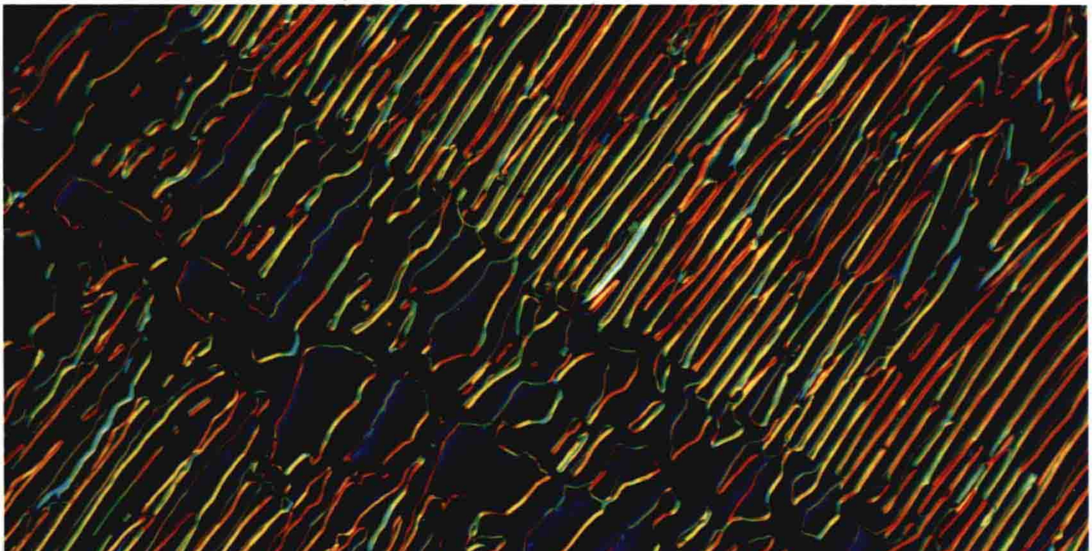
Corrosion Resistance Against Hydrogen



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Corrosion Resistance Against Hydrogen

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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 8,000 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.

Increasing demand for an English version of the DECHEMA-WERKSTOFF-TABELLE arose in the 1980s; accordingly 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 all information on the corrosion behavior of materials that are in contact with hydrogen or environments containing this gas. This compilation is an indispensable tool for all engineers and scientists dealing with corrosion problems in hydrogen containing environments of any industrial use.

About 90% of all hydrogen is commercially produced in petrochemical processes, e.g. by catalytic steam cracking (steam reforming) of natural gas (methane) or light crude oil fractions or by partial oxidation of heavy oil. Considerable amounts of hydrogen are also produced in numerous processes in refineries or coking plants as well as in electrochemical processes, such as chloralkali electrolysis. Hydrogen is used for numerous chemical processes, for example for the synthesis of ammonia and methanol as well as in hydrogenation processes such as for the production of gasoline or for fat hardening. In metal extraction processes (such as W, Mo, Co, etc) it is used as a reducing agent and is also used as a shielding gas for welding and metallurgical processes. Finally, it can be used as a fuel gas or can be liquefied and used as an aerospace fuel.

Corrosion is a complex phenomenon that depends on a number of parameters, related to both the environment and the metal. In this handbook the behavior of materials in contact with hydrogen containing gases and liquids is compiled.

The chapters are arranged by the agents leading to individual corrosion reactions, and a vast number of materials are presented in terms of their behavior in these agents. 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 the handbook.

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-to-day 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.

They are also indebted to Gudrun Walter of Wiley-VCH for her valuable assistance during all stages of the preparation of this book.

Michael Schütze, Günter Schmitt and Roman Bender

How to use the Handbook

The Handbook provides information on the chemical resistance and corrosion behavior of materials in hydrogen and hydrogen containing atmospheres.

The user is given information on the range of applications and corrosion protection measures for metallic, non-metallic inorganic, and organic materials, including plastics.

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 the different materials in contact with the medium.

The book is subdivided according to four groups of materials A-D:

- **A Metallic materials**
- **B Non-metallic inorganic materials**
- **C Organic materials and plastics**
- **D Materials with special properties**

These material groups are each subdivided according to their chemical formula; the metals are classed according to different alloy groups. These groups are shown in the uniformly designed summary table at the start of each chapter.

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.

Material recommendations are given for each of the four groups of materials and are summarized in the section:

- **E Material recommendations.**

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

In addition to the detailed descriptions, the corrosion resistance and chemical resistance of the materials is also summarized in a summary table at the start of the chapter. 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***[1] *x*		***Corrosion rate*** *y*
		g/(m²h)	***g/(m²d)***	***mm/a***
+	resistant	≤ 0.1	≤ 2.4	≤ 0.1[2]
⊕	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

1) Data applies to steel; for Al, Mg and their alloys, 1/3 of the value must be used
2) Values for Ta, Ti, and Zr are too high (*possible embrittlement due to hydrogen absorption in the event of corrosion*! Therefore, corrosion rate = 0.01 mm/a, see the individual cases)

The evaluation of the corrosion resistance of metallic materials is given

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

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

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

with x_1 in $g/(m^2h)$

$$\frac{x_1 \cdot 365 \cdot 24}{\rho \cdot 1000} = y(mm/a)$$

with x_2 in $g/(m^2d)$

$$\frac{x_2 \cdot 365}{\rho \cdot 1000} = y(mm/a)$$

where

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

In those media in which uniform corrosion can be expected, isocorrosion curves (corrosion rate y ≤ 0.1 mm/a) or resistance ranges for non-metallic materials are given where possible. The evaluation criteria for non-metallic inorganic materials are stated in the individual cases; depending on the material and medium, they may also be given as corrosion rates (mm/a).

If corrosion rate values are not given in the literature sources, then the resistance of the material is limited to the above mentioned resistance symbols. These resistance symbols are also used for the non-metallic inorganic materials and – if present in the literature – are supplemented by values for the corrosion rate.

The suitability of organic materials is generally evaluated by comparing property characteristics (e.g. mass, tensile strength, elasticity module or elongation at rupture) and other changes (e.g. cracking, swelling, shrinkage) after exposure to the medium with respect to these characteristics in the initial state before exposure. The extent of changes in the properties after exposure to the medium is decisive for the evaluation of the resistance to chemicals or the durability of the materials. The criteria listed below for the evaluation of the chemical resistance apply to thermoplastics used to manufacture pipes and are based on results from immersion tests with an immersion time of 112 days (see ISO 4433 Part 1 to 4). In principle, they are also applicable to other organic materials; however, they should be adapted to the individual material because, as the following table shows, the evaluation criteria are not consistent, even within a group of thermoplastics, but depend on the type of thermoplastic material.

Symbol	Meaning	Permissible limiting value[1]			
		of the mass change[2] %	of the tensile strength[3] %	of the elasticity module[3] %	of the elongation at rupture[3] %
+	resistant/durable	PE, PP, PB: –2 to 10 PVC, PVDF: –0.8 to 3.6	PE, PP, PB, PVC, PVDF: ≥ 80	PE, PP, PB: ≥ 38 PVC: ≥ 83 PVDF: ≥43	PE, PP, PB: ≥ 50 to 200 PVC, PVDF: 50 to 125
⊕	limited resistance/ limited durability	PE, PB, PB: > 10 to 15 or < –2 to –5 PVC, PVDF: < –0.8 to –2 or > 3.6 to 10	PE, PB, PB, PVC, PVDF: < 80 to 46	PE, PB, PB: < 38 to 31 PVC: < 83 to 46 PVDF: < 43 to 30	PE, PB, PB: < 50 to 30 or > 200 to 300 PVC, PVDF: < 50 to 30 or > 125 to 150
–	not resistant/not durable	PE, PP, PB: < –5 or > 15 PVC, PVDF: < –2 or > 10	PE, PP, PB, PVC, PVDF: < 46	PE, PP, PB: <31 PVC: < 46 PVDF: < 30	PE, PP, PB: < 30 or > 300 PVC, PVDF: < 30 or > 150

[1] The data applies to the values determined in the initial state without exposure to the medium which correspond to 100 %
[2] Relative mass change according to DIN EN ISO 175
[3] Tensile strength, elasticity module, and elongation to rupture according to DIN EN ISO 527-1
Scope of validity for PVC: PVC-U, PVC-HI, and PVC-C; for PE: PE-HD, PE-MD, PE-LD, and PE-X

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 incorrect 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 into account deliberately 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

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Warranty disclaimer

This book has been compiled from literature data with the greatest possible care and attention. The statements made in this chapter 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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Preliminary remarks

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