

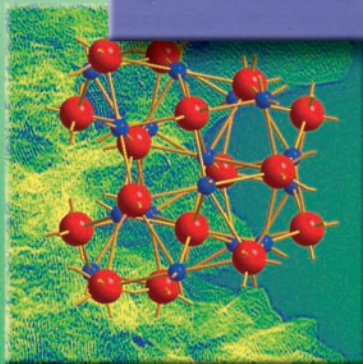
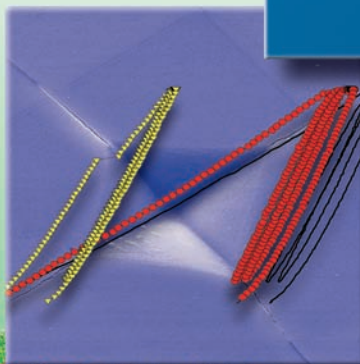
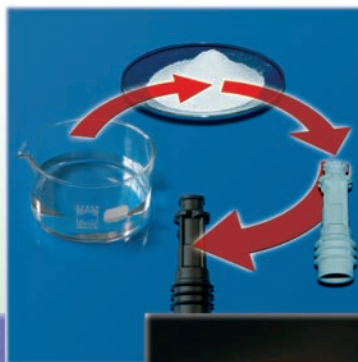
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Volume 4

Applications



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Editors

Prof. Dr. Ralf Riedel

TU Darmstadt
Institute for Materials Science
Petersenstr. 23
64287 Darmstadt
Germany

Prof. Dr. I-Wei Chen

University of Pennsylvania
School of Engineering
3231 Walnut Street
Philadelphia, PA 19104-6272
USA

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Preface

Along with metals and polymers, advanced ceramics are one of the most promising classes of materials for the key technologies of the 21st century. Recent developments in the field has resulted in a number of new synthesis, processing and sintering techniques for the production of novel structural and functional ceramics and ceramic composites. Significant progress has also been made in the past two decades in the production of novel multifunctional ceramics with a tailor made micro- and/or nanoscale structure to respond to the increasing technological demand for advanced ceramic materials.

The four-volume series of Ceramics Science & Technology covers various aspects of modern trends in advanced ceramics reflecting the status quo of the latest achievements in ceramics science and development. The contributions highlight the increasing technological significance of advanced ceramic materials and present concepts for their production and application. Volume 1 deals with structural properties of ceramics by considering a broad spectrum of length scale, starting from the atomic level by discussing amorphous and crystalline solid state structural features, and continuing with the microstructural level by commenting on microstructural design, mesoscopic and nano structures, glass ceramics, cellular structures, thin films and multiphase (composite) structures. Volume 2 focuses on i) various distinct classes of ceramic materials, namely oxides, carbides and nitrides, and ii) physical and mechanical properties of advanced ceramics. The series is continued with Volume 3 with chapters related to advanced synthesis and processing techniques used for the production of engineering ceramics and is here completed by Volume 4 which is devoted to applications of engineering and functional ceramics.

Quo vadis ceramics? The four-volume series intends to provide comprehensive information relevant to the future direction of ceramics. In this respect, Volume 4 describes commercial applications of several advanced, engineering ceramics to offer evidence for their technological importance and to point to trends for the further development of this fascinating class of materials. Latest examples of commercial ceramics are found in transportation industry: PZT ($\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$)-based piezoelectric actuators and Si_3N_4 -based ball bearings and glow plugs are used in diesel engines, carbon fiber reinforced silicon carbide (C/SiC) is used for brakes, and oxide ceramics-based thermal barrier coatings are used in jet engines; in lighting

industry: sialon-derivative-based luminescent ceramics for LED applications, and GaN-based ceramics for optoelectronics; and in many others.

As novel ceramics are called for and expected to establish a commercial status in the future in a number of emerging application fields, there is the need for a long-term alignment with the emerging fields and for continued fundamental research in ceramics science and technology. Along this line, Volume 4 highlights potential applications of advanced ceramics in applications such as fuel cells, membranes, gas sensors, and energy storage. In addition, specific functions uniquely delivered by ceramic materials are described: nanostructured ceramics for superhard applications, ceramics for ultrahigh temperature and corrosive environment applications, and ceramics for magnetic and microwave applications. Finally, novel compositions based on polymer-derived ceramics and nitridosilicates are discussed as promising future materials with properties unmatched by any material known today and ones that can only be realized by designing the material structure at the nanoscale. In this way, we hope this final volume and the four-volume series will celebrate and contribute to the exciting development of ceramics and technology by providing the latest scientific knowledge to ceramic students and ceramic research community.

We wish to thank all the contributing authors for their great enthusiasm in compiling excellent manuscripts in their respective area of expertise. We also acknowledge the support of the Wiley-VCH editors, Bernadette Gmeiner and Martin Preuß, for their continuous encouragement to work on this project.

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Ralf Riedel
I-Wei Chen

List of Contributors

Jörg Adler

Fraunhofer Institute for Ceramic
Technologies and Systems
Winterbergstrasse 28
01277 Dresden
Germany

Lambert Alff

Technische Universität Darmstadt
Institute of Materials Science
Petersenstr. 23
65287 Darmstadt
Germany

Natalia N. Bramnik

Karlsruher Institut für Technologie
(KIT)
Institut für Angewandte Materialien-
Energiespeichersysteme (IAM-ESS) &
Institut für Anorganische Chemie
Hermann-von-Helmholtz-Platz 1
76344 Eggenstein-Leopoldshafen
Germany

Paolo Colombo

University of Padova
Dipartimento di Ingegneria Meccanica
Settore Materiali
35131 Padova
Italy

and

The Pennsylvania State University
Department of Materials Science and
Engineering
University Park, PA 16802
USA

Helmut Ehrenberg

Karlsruher Institut für Technologie
(KIT)
Institut für Angewandte Materialien-
Energiespeichersysteme (IAM-ESS) &
Institut für Anorganische Chemie
Hermann-von-Helmholtz-Platz 1
76344 Eggenstein-Leopoldshafen
Germany

Aleksander Gurlo

Technische Universität Darmstadt
Fachbereich Material- und
Geowissenschaften
Petersenstr. 32
64287 Darmstadt
Germany

Naoto Hirosaki

National Institute for Materials Science
(NIMS)
Namiki 1-1, Tsukuba
Ibaraki 305-0044
Japan

Peter Holtappels

Technical University of Denmark
Department of Energy Conversion
and Storage
Frederiksborgvej 399,
4000 Roskilde
Denmark

Pavel Holubář

SHM s.r.o.
Průmyslová 3
787 01 Šumperk
Czech Republic

Nathan S. Jacobson

NASA Glenn Research Center
MS 106-1, 21000 Brookpark Road
Cleveland, OH 44135
USA

Boštjan Jančar

Jožef Stefan Institute
Advanced Materials Department
Jamova 39
1000 Ljubljana
Slovenia

Allan P. Katz

Air Force Research Laboratory
Materials and Manufacturing
Directorate, AFRL/RXCC
Wright-Patterson AFB, OH 45433-7817
USA

Ronald J. Kerans

Air Force Research Laboratory
Materials and Manufacturing
Directorate, AFRL/RXCC(Emeritus)
Wright-Patterson AFB, OH 45433-7817
USA

Ralf Kriegel

Fraunhofer Institute for Ceramic
Technologies and Systems
Michael-Faraday-Str. 1
07629 Hermsdorf
Germany

Gabriela Mera

Technische Universität Darmstadt
Institute for Materials Science
64287 Darmstadt
Germany

Mamoru Mitomo

National Institute for Materials Science
(NIMS)
Namiki 1-1, Tsukuba
Ibaraki 305-0044
Japan

Takeshi Mitsuoka

NGK Spark Plug Co., Ltd
Material Research Dept R&D Center
2808 Iwasaki Komaki-shi
Aichi 485-8510
Japan

Sandro Pagano

Ludwig-Maximilians-University
Munich
Department of Chemistry
Butenandtstrasse 5-13
81377 Munich
Germany

Elizabeth J. Opila

University of Virginia
Department of Materials Science and
Engineering
395 McCormick Rd.
Charlottesville, VA 22904
USA

Ralf Riedel

Technische Universität Darmstadt
Institute for Materials Science
64287 Darmstadt
Germany

Wolfgang Schnick

Ludwig-Maximilians-University
Munich
Department of Chemistry
Butenandtstrasse 5–13
81377 Munich
Germany

Gian Domenico Soraru

University of Trento
Materials Science and Technology
38122 Trento
Italy

Bhaskar Reddy Sudireddy

Technical University of Denmark
Department of Energy Conversion and
Storage
Frederiksborgvej 399,
4000 Roskilde
Denmark

Danilo Suvorov

Jožef Stefan Institute
Advanced Materials Department
Jamova 39
1000 Ljubljana
Slovenia

Robert Vaßen

Forschungszentrum Jülich
Institut für Energieforschung
Wilhelm-Johnen-Straße
52425 Jülich
Germany

Stan Vepřek

Technical University Munich
Department of Chemistry
Lichtenbergstr. 4
85747 Garching
Germany

Maritza G.J. Vepřek-Heijman

Technical University Munich
Department of Chemistry
Lichtenbergstr. 4
85747 Garching
Germany

Ingolf Voigt

Fraunhofer Institute for Ceramic
Technologies and Systems
Michael-Faraday-Str. 1
07629 Hermsdorf
Germany

Marcus Weyd

Fraunhofer Institute for Ceramic
Technologies and Systems
Michael-Faraday-Str. 1
07629 Hermsdorf
Germany

Rong-Jun Xie

National Institute for Materials Science
(NIMS)
Namiki 1-1, Tsukuba
Ibaraki 305-0044
Japan

Martin Zeuner

Ludwig-Maximilians-University
Munich
Department of Chemistry
Butenandtstrasse 5–13
81377 Munich
Germany

Part One

Structural Applications

1

Oxidation and Corrosion of Ceramics

Elizabeth J. Opila and Nathan S. Jacobson

1.1

Introduction

Ceramics are compounds with strong covalent or ionic bonds, typically rendering them very stable with high melting points. While oxides in oxidizing environments are quite stable at high temperatures, carbides, nitrides, and borides are all less thermodynamically stable than their corresponding oxides. For this reason, the reaction of non-oxide ceramics to form oxides is a very important problem in many high-temperature environments. These types of reactions are important for structural ceramics used in a wide variety of applications including furnaces, engines, land-based turbines for power generation, heat-exchangers, hot-gas filters, chemical process containers, and re-entry shields. In addition, non-oxide ceramic materials are often used as substrates in high-temperature functional devices such as sensors, actuators, and fuel cells wherein environments can also be oxidizing.

The oxidation and corrosion of many technologically important ceramics are detailed in this chapter, with emphasis placed on the reactions of non-oxide ceramics. Classes of ceramics with the same cation are considered together. Silica formers, alumina formers, and then hafnia and zirconia formers are discussed explicitly. The effects of carbon, nitrogen and boron on the formation of the more stable condensed phase oxides are also discussed. Within each section, the ideal oxidation reaction is discussed first, after which complications due to complex materials and complex environments are considered. Finally, a short discussion of oxide degradation is provided.

Emphasis is placed on the thermodynamics and kinetics of the oxidation and corrosion reactions with the aim of describing the current capability to predict the rate of material degradation. Areas requiring additional elucidation are noted. Generally, at moderate temperatures the rate of material degradation is limited by the surface reaction of the material with its environment; the reactions are thus sensitive to the processing, crystal structure and orientation of the ceramic. At higher temperatures, however, the degradation rate is typically diffusion-controlled, and under these conditions the reaction rate is controlled by reactant or product transport through the growing oxide, or vapor transport through a gaseous boundary layer. These reaction mechanisms are shown schematically in Figure 1.1.

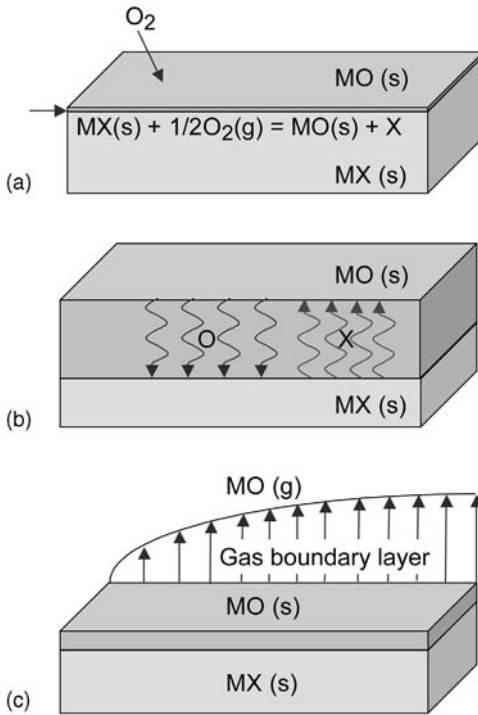


Figure 1.1 Rate-limiting material degradation mechanisms. (a) Reaction-limited oxidation; (b) Solid-phase diffusion-limited oxidation; (c) Gas-phase diffusion-limited volatilization.

1.2

Silica-Forming Ceramics

Silicon carbide (SiC) and silicon nitride (Si₃N₄) are two ceramic materials that show promise for long-term, high-temperature applications due to the formation of a slow-growing protective silica film that forms in oxidizing environments. Extensive studies have been made of the oxidation and corrosion of SiC and Si₃N₄, as reviewed previously [1,2]. Consequently, much of this chapter will cover these materials, with ideal behavior being discussed first in this section. Complications for real materials in real environments are then presented.

1.2.1

Ideal Oxidation Behavior of Silica-Forming Ceramics

1.2.1.1 Structure of Silica and Transport of Oxygen in Silica

In order to understand the oxidation of silica-formers, the structure of silica must first be discussed (the reader is referred to an in-depth review by Lamkin, Riley, and Fordham [3] for a more detailed discussion of this topic). Silica exists in several

polymorphs, the amorphous phase, and the crystalline phases. The crystalline phases are – from the low-temperature polymorphs to the high-temperature polymorphs – quartz, tridymite, and cristobalite, respectively. Amorphous silica is composed of an irregular network of SiO_4 tetrahedra. A two-dimensional (2-D) representation of amorphous silica is shown in Figure 1.2a, with rings of varying numbers of Si–O bonds. Figure 1.2b shows a 2-D representation of crystalline silica in which the structure is ordered into six-member rings of Si–O bonds. The density of cristobalite (2.32 g cm^{-3}) is closest to amorphous silica (2.20 g cm^{-3}). Both, the amorphous phase and cristobalite have a relatively open structure that allows the permeation of molecular oxygen through the interstices of the structure. Figure 1.2c shows the case where the silica network has been modified by cations incorporated in the interstices of the glass structure. These modifying cations, which typically are the alkali metals and alkaline earths, are charge-compensated by the formation of non-bridging oxygen. The glass network is thus disrupted by the incorporation of these cations, which then affects transport of oxidant through the silica.

The transport of oxygen through silica can occur by several mechanisms: (i) by molecular permeation through the interstices of the structure; and (ii) by the exchange of oxygen ions with the network oxygen. The permeability of oxygen in silica has been measured by Norton [4], and shown to be a product of the diffusivity and the solubility of oxygen in silica. Norton showed that the rate of permeation was proportional to the first power of the pressure, thus indicating that molecular oxygen was the diffusing species. Several ^{18}O tracer diffusion studies of oxygen transport in silica have also been conducted, but only some of the more recent are detailed here [5,6]. In these studies, the exchange of oxygen with the silica network – which is slower than that of oxygen permeation – is measured. Thus, the oxidation of silica-formers is expected to be dominated by rates of permeation of molecular oxygen through the silica interstices. This transport mechanism will be discussed in the following sections.

1.2.1.2 Oxidation of Silicon in Dry Oxygen

A discussion of the oxidation of silicon is included here for two reasons. First, oxidation occurs by a simple reaction without the formation of any products except silica:



Second, this reaction has been studied extensively due to its application for semiconducting microelectronics.

The classic study for the oxidation of silicon is that of Deal and Grove [7], which makes several important points. First, the overall oxidation reaction kinetics for silicon can be described by the relationship:

$$x_o^2 + Ax_o = B(t + \tau) \quad (2)$$

where x_o is the oxide thickness, t is time, τ is a shift in time that corrects for the presence of any native oxide layer, and A and B are constants. At short times, or for

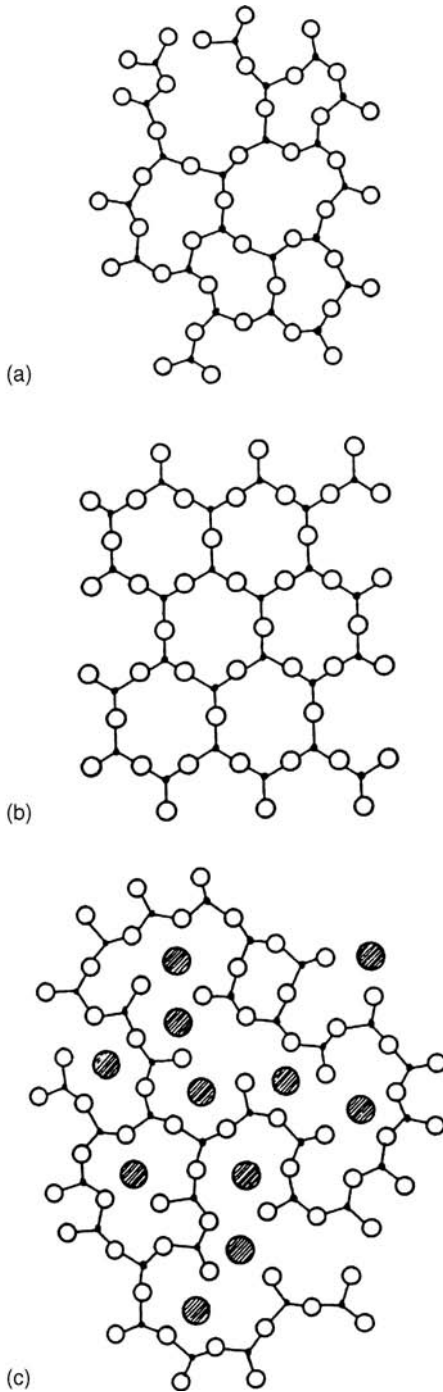


Figure 1.2 Schematic structure of silica. (a) Amorphous silica; (b) Cristobalite; (c) Alkali-modified silica. Silicon atoms are represented by small dark circles, oxygen atoms by open

circles, and alkali impurities as large cross-hatched circles. Reproduced with permission from Ref. [3]; © 1992, *Journal of the European Ceramic Society*.

thin oxide scales, the relationship reduces to a linear rate law:

$$x_o \cong B/A (t + \tau) \quad (3)$$

where B/A is the linear rate constant. Here, the oxidation rate is controlled by the reaction of the oxidant with the substrate at the oxide/substrate interface. At long times, and for thick oxide scales, Eq. (2) reduces to

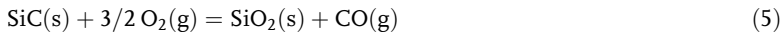
$$x_o^2 \cong Bt \quad (4)$$

where B is the parabolic rate constant. (Note: While Deal and Grove use the symbol B , the oxidation community generally uses the symbol k_p to represent the parabolic rate constant.) In the case of parabolic oxidation, oxidation is limited by transport of the oxidant through the silica scale, and the oxidation rate slows parabolically with time as the scale thickens. Linear kinetics are observed at low temperatures and short times, whereas parabolic kinetics are observed at long times and high temperatures. Under intermediate conditions the complete expression (Eq. (2)) must be used. The complete expression and the transition between the two limiting cases (Eqs (3) and (4)) are shown in Figure 1.3. These oxidation kinetics can be determined by either measuring weight gain due to silica formation or by measuring the oxide thickness.

Another important result of the Deal and Grove [7] study was that the activation energy (E_a) for the oxidation of silicon (119 kJ mol^{-1}) was in agreement with the E_a for the molecular permeation of oxygen through silica of 113 kJ mol^{-1} , as measured by Norton [4]; this indicated that the mechanism of oxygen transport was the same. In addition, Deal and Grove found that the parabolic oxidation rate constant was proportional to the first power of the oxygen pressure, indicating that molecular oxygen is the diffusing species.

1.2.1.3 Oxidation of Silicon Carbide in Dry Oxygen

The oxidation of SiC is expected to be similar to that of silicon, since the only solid oxidation product is silica. However, in this case, the carbon is also oxidized to form gaseous carbon monoxide:



Results for the oxidation of chemical vapor deposited (CVD) SiC show many similarities to silicon oxidation. First, at lower temperatures, linear kinetics are important [8], while at higher temperatures ($\geq 1200^\circ\text{C}$) parabolic kinetics are adequate to describe oxidation under most conditions [9]. Second, the E_a for parabolic oxidation [9] (118 kJ mol^{-1}) agrees with that of Norton [4] and Deal and Grove [7], as shown in Figure 1.4. This suggests that molecular oxygen permeation through the growing silica scale limits the oxidation rate.

There are a number of differences for the oxidation of SiC compared to that of silicon that should be mentioned. First, the linear rate constants for SiC are in general lower than those of silicon [8]. The reaction of oxygen at the substrate surface will be different due to the presence of C. Second, the parabolic rate constant is expected to be 1.5- to 2-fold lower for SiC than for Si, since additional oxygen is used

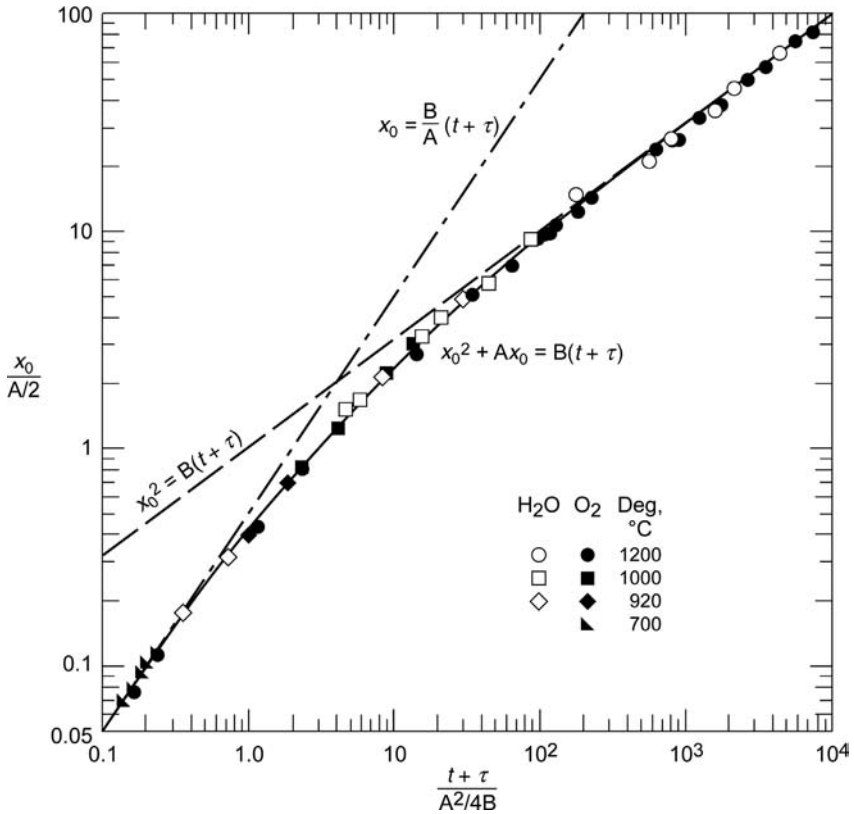


Figure 1.3 General linear-parabolic oxidation kinetics showing the limiting linear kinetics at short times/thin oxide scales and limiting parabolic kinetics at long times/thick oxide scales. Reproduced with permission from Ref. [7]; © 1965, The American Institute of Physics.

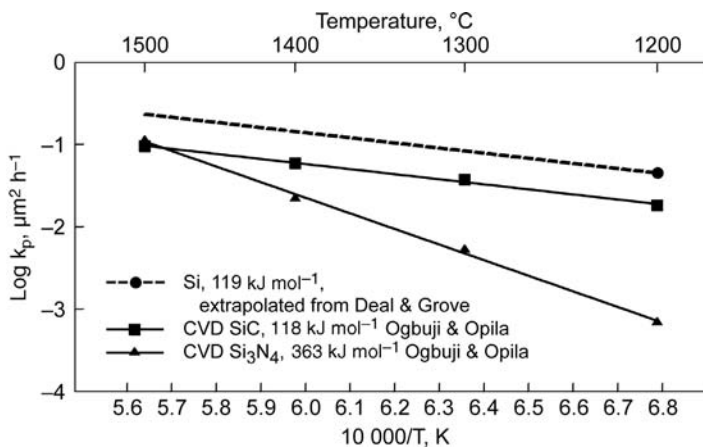


Figure 1.4 Parabolic oxidation rates of pure silicon, SiC and Si₃N₄ in dry oxygen. Reproduced with permission from Ref. [10]; © 2000, Wiley-VCH Verlag GmbH & Co. KGaA.