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Preface

Chemical and physical basics paired with engineering "black box" concepts as well as practical and theoretical experience in conventional and advanced ceramics paired with unorthodox ideas for future materials are the humus of the book in hand. On the one hand, it is a guideline for students, scientists, and engineers, and on the other hand, it presents ideas for visionaries. It is the alliance of a view into the past, the present, and the future. Not more, not less. May the readers have exactly the same pleasure with the book in hand as we have had with its creation.

The book is based upon lectures/papers/posters that are held/published/presented at/from the Department Aldinger of the Max-Planck-Institut für Metallforschung (Germany) and the Chair Aldinger on Nichtmetallische-Anorganische Materialien of the Universität Stuttgart (Germany) during the past decades – joint institutions which became also known as "Pulvermetallurgisches Laboratorium (PML)". A selection of these works is accumulated in [76]–[189]. Some of the knowledge of [76]–[189] is used as "case studies" in the book. We truly regret that it was not possible to include all works that were done at the "Pulvermetallurgisches Laboratorium (PML)" during that time. Nevertheless, we hope that most of the readers consider the selection of works presented in this book satisfactory. Furthermore, we hope that most of the readers consider our decision to discuss ceramic materials within an extended frame of reference, which also incorporates metallic materials and organic materials, satisfactory. Moreover, we hope that at least some of our readers agree with us that it is a good time to carry out first steps towards future materials paving the way to artifical gravitation technologies and energy production technologies that go beyond chemical and nuclear reactions – exactly this is what we want to do in the final chapter of the book.

We wish to thank Dorothee Klink for the proofreading, Bernd Heinze for supplying us with nice photographs, CeramTec [71] for the abandonment of product images, microstructure images, and pictures of technical facilities, and SGL Brakes GmbH [72] for the release of images of ceramic (carbon) brake discs. Furthermore, we would like to thank Joachim Bill and Jerzy Golczewski for their valuable help. Moreover, the coauthor would like to thank Arndt Simon and Jürgen Köhler for the stimulating time at the Department Simon of the Max-Planck-Institut für Festkörperforschung.

Fritz Aldinger und Volker A. Weberruß,
Stuttgart, January 2010.

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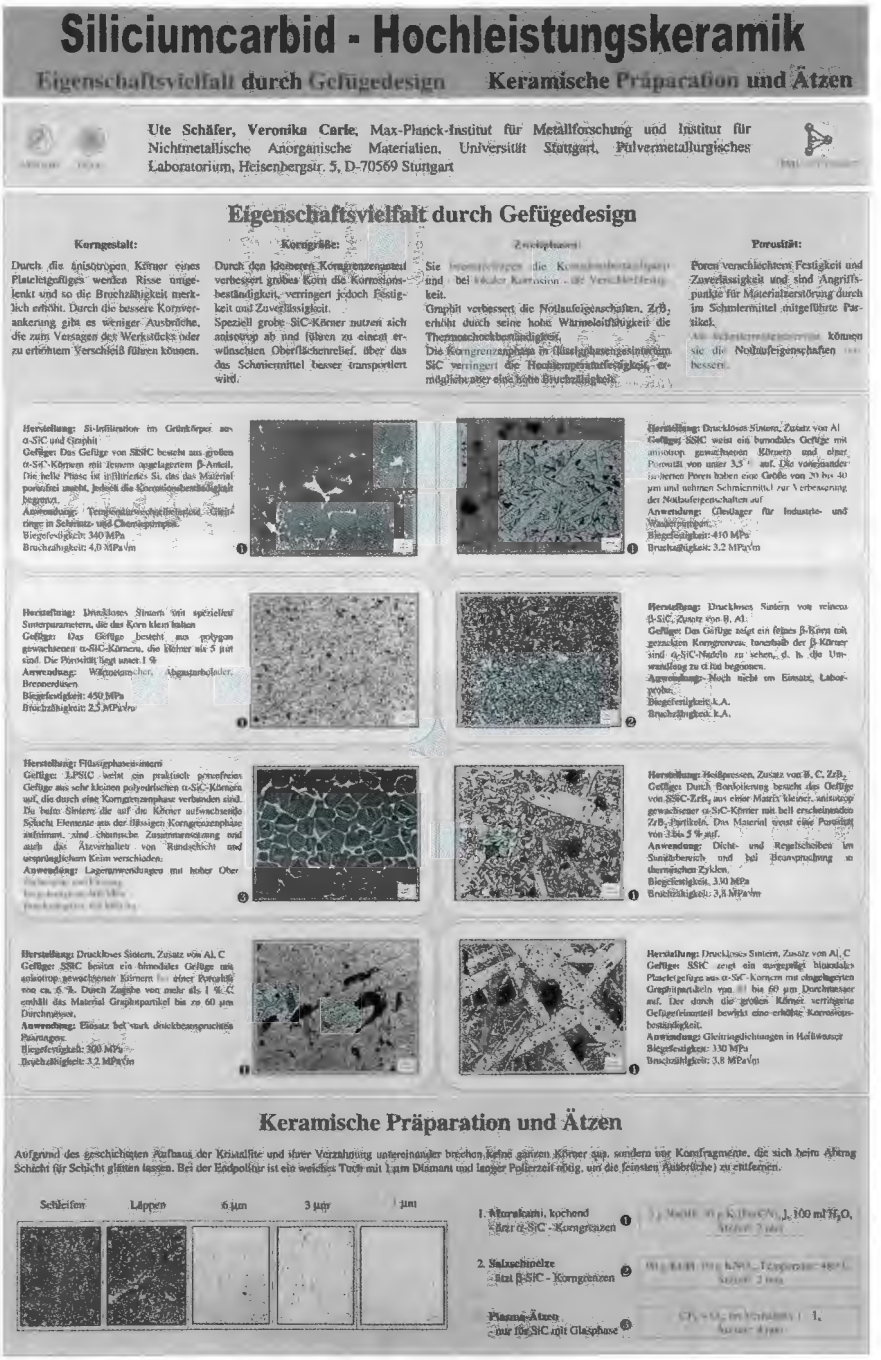


Max-Planck-Campus, Stuttgart (Germany)



Max-Planck-Institut für Metallforschung,
Pulvermetallurgisches Laboratorium (PML)

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Silicon carbide materials.

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Synthese metallorganischer Polymere als molekulare Vorstufen für hochtemperaturstabile Keramiken

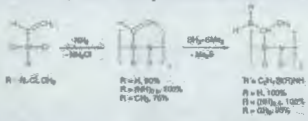
Markus Weinmann, Anita Müller, Peter Gerstel, Thomas W. Kamphowe, Sabine Nast, Joachim Bill und Fritz Aldinger

Max-Planck-Institut für Metallforschung und Institut für Nichtmetallische Anorganische Materialien, Universität Stuttgart, Pulvermetallurgisches Laboratorium, Heisenbergstr. 5, D-70569 Stuttgart (Germany)

Hintergrund: Keramiken aus molekularen Vorstufen im System Si-B-C-N können außergewöhnliche Hochtemperaturstabilitäten bis über 2000°C aufweisen. Die Synthese der Polymere sowie der Einfluß der polymeren Strukturen auf die thermische Stabilität der Keramiken wurde bisher nur wenig untersucht. In diesem Zusammenhang hat sich die Darstellung neuer Präkeramika als einer unserer Arbeitsschwerpunkte entwickelt, wobei insbesondere prozeßrelevante Fragestellungen wesentliche Aspekte bei der Entwicklung neuer Synthesen darstellen.

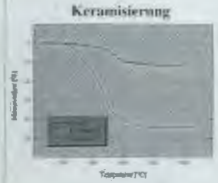
Hydroborierung vinylierter Polysilazane

Ziel: Synthese hochvernetzter Polysilazane in hoher Ausbeute



Resultat: Hohe Produktausbeute, einfache Durchführung, Ansätze beliebig zu vergrößern.

Keramisierung



TGA von $\{B(C_2H_3)_2\text{-}Si(R)NH\}_3$, Heizrate 2°C/min, Argon

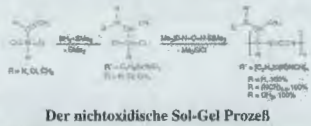
Hochtemperaturverhalten



HT-TGA der $\{B(C_2H_3)_2\text{-}Si(R)NH\}_3$, Kompaktes (1400°C), Heizrate 2°C/min, Argon

Bormodifizierte Polysilylcarbodiimide

Ziel: Prozeßführung ohne unlösliche Nebenprodukte

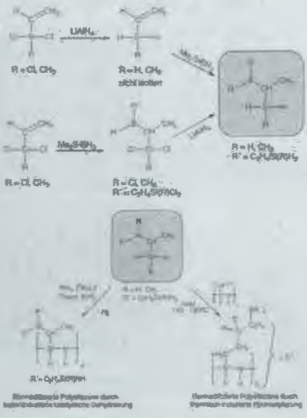


Der nichtoxidische Sol-Gel Prozeß



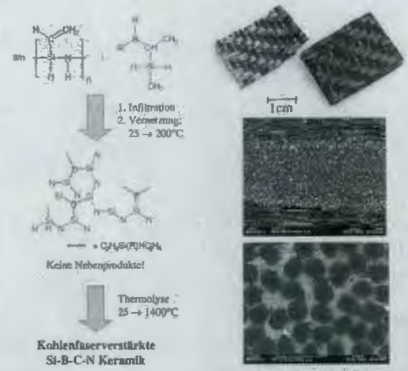
Tris(hydridosilylethyl)borane: Hochreaktive Edukte für Si-B-C-N Precursor

Ziel: Synthese neuer Synthone für die Herstellung hochvernetzter Si-B-C-N Polymere aus monomeren Vorstufen



Duroplastische Präkeramika

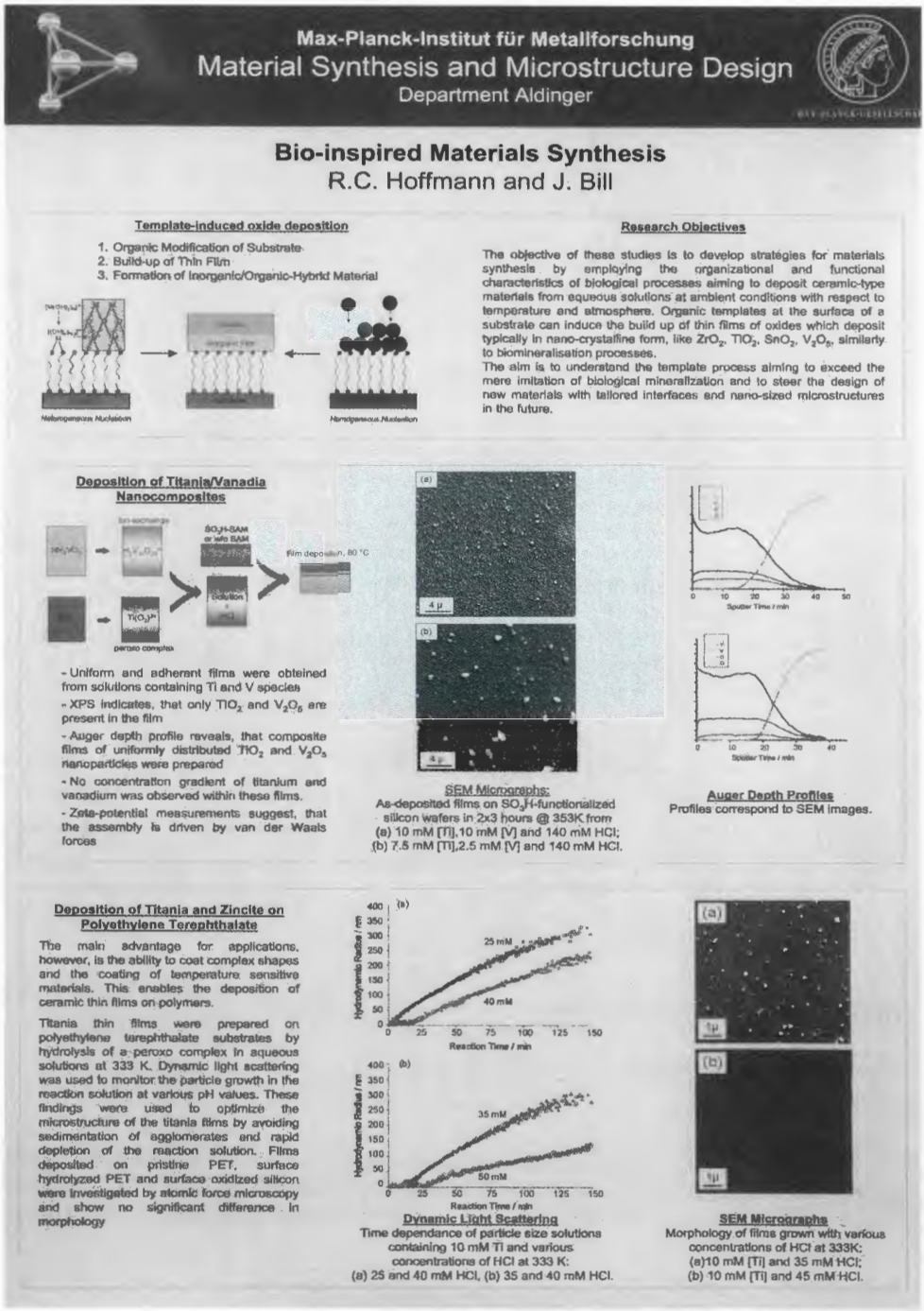
Ziel: Herstellung faserverstärkter Komposit-Materialien mit hochtemperaturstabiler Matrix mittels RTM-Verfahren



Kohlenfasergewebe vor und nach Infiltration (oben links bzw. rechts). Mitte und unten: REM Aufnahmen eines Schliffs der kohlenfaserverstärkten Si-B-C-N Keramik bei 500- und 3000-facher Vergrößerung.

Precursor-derived materials.

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Bio-inspired materials.

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Defining Ceramics

1. Advanced Ceramics

What would the ancient China have been without china? Imperfect! What would be the life of today without dental prostheses? Painful! What would be the space shuttle without thermal tiles? Disastrous! What would be the daily communication without mobile phones? Unimaginable! Is it thus carrying things too far that ceramic materials are objects of technologies of the past, the present, and the future? No way! But what are ceramic materials actually? Which structure do they have? How are their properties related to their structure? How are these manufactured? How are these modeled? Going somewhat beyond the conventional textbooks and the conventional monographs on modern ceramics, in the chapters that follow, an elaborate picture of modern ceramics is developed.

Going beyond the hellenic word *keramos* ("fired soil"), on the one hand, *ceramics* is defined as a name for products made out of non-metallic inorganic substances, and on the other hand, *ceramics* is defined as the art and science of making materials and products of non-metallic inorganic substances [28]. Naturally, following the standards of modern physics and modern chemistry, we want to associate the notion *non-metallic* with non-metallic energy band structures and their dependence on further constraints such as temperature and pressure, and we want to associate the notion *inorganic* with substances not showing the chemical structures of hydrocarbons. Certainly, we want to appreciate *conventional ceramics*, but we want to focus on *advanced ceramics*. We here compare with Figure 1.1, which shows the classifications, the definitions, and the terminology used in this book, and we here compare with Figures 1.2–1.13, which show some selected starting materials as well as some selected products of various branches of the ceramic industry.

We should already here appreciate that advanced ceramics meets the highest demands of present technologies. For instance, many ceramic materials are extremly resistant against abrasion! For instance, many ceramic materials are extremly resistant against heat! For instance, depending on further constraints such as temperature and pressure, ceramic materials can be insulators, ceramic materials can be conductors, and ceramic materials can be semi-conductors. Dear reader, ceramic materials even can be ferroelectrics without which the performance of present communication technology would be more than poor. Dear reader, the hip joint endoprostheses that are shown in Figure 1.10 are implants meanwhile doing their job in hundreds of millions of human bodies worldwide! Isn't this a feat?

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Figure 1.1. Classifications, definitions, and terminology. * frequently noted as "fine ceramics" (Japan) or "Hochleistungskeramik" (Germany). ** frequently noted as "engineering ceramics" (USA, GB) or "Ingenieurkeramik" (Germany).



Figure 1.2. Mineral stones and powdered artifical non-metallic inorganic materials.

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aluminium oxide (Al_2O_3)

Figure 1.3. Laboratory ware.

images kindly provided by CeramTec



magnesium silicate
($Mg_3Si_4O_{10}$ hydroxide: steatite)



aluminium oxide (Al_2O_3)

Figure 1.4. Grinding balls.



Tribofil®
(CeramTec)

images kindly provided by CeramTec

Figure 1.5. Textile machinery components. Pigtails (top) and aller guides (bottom).



ZN 101 B
(CeramTec)

TZP (ZrO_2), Y_2O_3 stabilized

images kindly provided by CeramTec

Figure 1.6. Ceramic cutters. Scissors (top) and knives (bottom).

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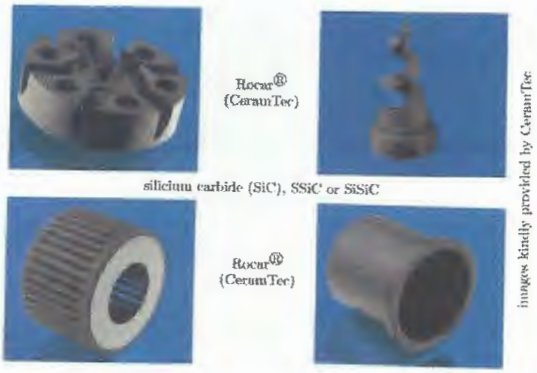


Figure 1.7. Components for industrial machinery and industrial facilities. SSiC: sintered SiC, SiSiC: Si-infiltrated SiC.

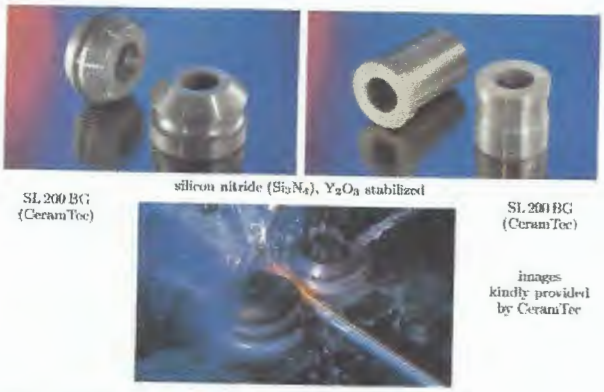


Figure 1.8. Welding rollers (top) and their application (bottom). The lower picture shows a facility for pipe welding.





Figure 1.9. Centering pins for welding processes (top) and their application (bottom). The lower picture shows a facility for metal active gas welding.

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Figure 1.10. Hip joint endoprosthesis (top) and its application (bottom).

image kindly provided
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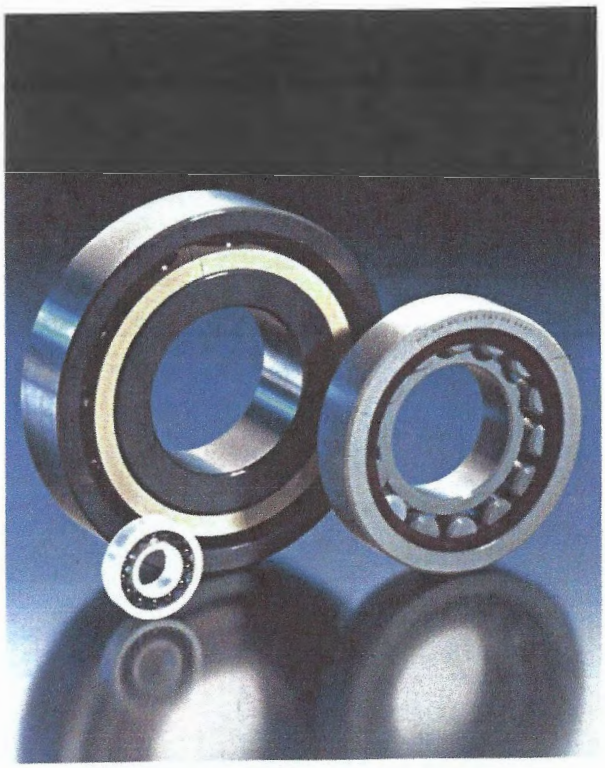


Figure 1.11. Ball (roller) bearings.

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brake disc with stainless steel bell



images kindly provided by SGL Brakes GmbH

brake disc with titanium bell

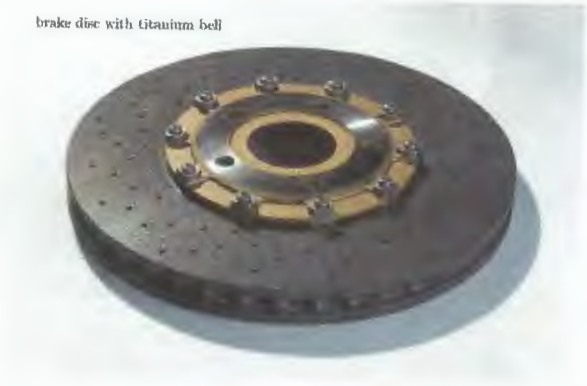


Figure 1.12. Ceramic (carbon) brake discs.

taken from the VAW:e picture archive



Figure 1.13. PC motherboard with chip carriers.

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Going beyond advanced ceramics, in the final Chapter 5, first steps towards new fields of materials research are carried out. The following first introductory remarks already here should be useful. On the one hand, a branch of research is started up dealing with the question "How must materials be structured and how must their technical environment be structured that these can be used as the material basis for an oscillatory system generating a measurable oscillatory gravitational field, so to speak, as the material basis for a gravitational laser?" On the other hand, a branch of research is started up dealing with the question "How must materials be structured and how must their technical environment be structured that these – fundamentally going beyond nuclear techniques and matter–antimatter destruction – can be disaggregated into radiation, which in turn can be used as starting point for new types of energy plants, new types of spacecraft propulsions, and new types of matter conversion techniques?" For this purpose, a self-consistent network of model conceptions is launched, which some colleagues may consider as a direct extension of the Ginzburg–Landau theory of superconductivity [20] or as a semi-classical approach to quantum systems comparable to the Wunner–Main approach to quantum systems [34, 35, 64], however, which could turn out to be the true nonlinear extension of conventional quantum mechanics [63], on all accounts, which works without any known restrictions, and which firstly can supply us with much more information about the principles that govern the constitution, the stabilities, and the instabilities of materials than the methods of thermodynamics and the methods of quantum mechanics can do, and which secondly can supply us with paths to these new fields of materials research. Certainly, it goes far beyond the scope of this book to develop these new fields of research in great detail already here. However, the first steps towards this goal indeed are taken here.

Why do we think that a book about advanced ceramics is the adequate place for such first steps? Well, on the one hand, in the framework of advanced fuels such as nuclear fuel rods, ceramic materials play an important role so that we expect that ceramic materials will also play an important role in our more advanced context. Well, on the other hand, wanting to gain an access to artifical gravitation, it should not be the worst choice to depart from materials with a relatively high mass density and a relatively low free charge carrier density, promising us high gravitational radiation and low electromagnetic radiation, as it is the case for a lot of ceramic materials. Anyway, departing from advanced ceramics of the past and the present, let us also point into the future of materials.

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EXHIBIT OOO

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KINGERY

INTRODUCTION TO CERAMICS



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Introduction to Ceramics

by

W. D. Kingery

ASSOCIATE PROFESSOR OF CERAMICS
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

John Wiley & Sons, Inc., New York · London

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Library of Congress Catalog Card Number: 60–53448

Printed in the United States of America

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Preface

The need for a book such as this one has been impressed on me by my experience in teaching and studying ceramics; my appreciation of this need has been strengthened by numerous contacts with industrial and research scientists and ceramic production engineers. The basis of the book can for the most part be expressed in the idea that ceramics are better considered as a *class of materials* than the product of a special industry. This contention is reinforced by the fact that most of the new ceramic products of the last twenty years have been developed through the efforts of users rather than by the traditional ceramic industry.

The present book does not discuss ceramic *engineering* as such. However, it is clear that the engineer must understand ceramic materials and ceramic processes as a basis for engineering applications. Although it would be a great advantage to have available a text which considered ceramic processes and ceramic engineering from a general point of view, engineers entering the ceramic industry cannot afford to do without the principles required as a basis for that subject. Mere familiarity with current engineering practices is not sufficient; recently this was made clear when many pottery manufacturers found it expedient to enter new product areas such as dielectrics, magnetic ceramics, and optical ceramics.

Scientists and engineers realize more and more that many of the compartments into which knowledge is divided and the barriers between them are artificial and are based largely on ignorance. For example, separate discussions of glass formers as applied to volcanic ash, porcelain enamels, ceramic glazes, frit porcelains, encapsulating

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compositions, optical glass, container glass, etc., are clearly inefficient. The lack of general understanding thirty years ago led to traditional divisions of course structure and subject content; these divisions can no longer be justified. An empirical approach to ceramic technology was necessary in the past and could not possibly be avoided because ceramic systems are complex and were but poorly understood; this is no longer true today.

All the standard ceramics included in separate discussions of glass, body formulation, electrical ceramics, refractories, abrasives, glaze compositions, etc., are included here; they have been brought in as illustrative material at points where science and technology dictate what these compositions are rather than as separate branches of the industry. For example, compositions of triaxial whiteware porcelains are determined by (*a*) requirements for forming, (*b*) requirements for successful firing, (*c*) requirements for final properties, and (*d*) economic considerations. In this text whitewares are brought in under these subject categories rather than by treating them as a separate topic. The opportunities for teachers or readers to include additional examples and illustrations from their own experience will be apparent.

In a broader sense the same sort of compartmentalization that is artificial in ceramic technology is so for materials study in general. Divisions into metallurgy, ceramics, and plastics technology are rapidly approaching the end of their usefulness. Students using this book will, I hope, someday look back and view it as being too parochial. I have tried to encourage the development of this point of view in the text and consider it as a certain future development. In my view an ideal arrangement for studying materials science and engineering would be for undergraduates to study the broad principles of chemical and physical separations, material properties, and materials processing. Specialization in ceramics, ceramic engineering, metallurgy, metallurgical engineering, plastics technology, etc., should come only in the final year. So far as I am aware, this is nowhere being done in 1960, although it is the object of much discussion at various universities.

This book in mimeograph form has been used at the Massachusetts Institute of Technology as the text for two subjects in ceramics. Parts III and IV form the basis of a one-term subject for undergraduate juniors or seniors who have had a previous introduction to physical metallurgy and are thus familiar with the first principles of crystal structure and phase diagrams. Without this preparation, two terms would be required to cover the same material adequately. Most students have had a previous course in ceramic processes, but this is not

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required. Material included in Part V forms the major part of a course on physical ceramics designed principally for graduate students; seniors with good records are allowed to attend and have done well. There is some feeling that a two-term sequence with Chapters 19 and 20 taken up separately would have advantages.

In preparing the text a considerable amount of material was included that had been but recently investigated and reported in the technical literature, with the disadvantage that some of it will have to be changed as our understanding and interpretation improve. However, much of this material is important for current and developing applications of ceramics. I have freely included my own opinions, many of which have not been proved and may change in the future.

This book is really the product of many individuals who have kindled, sustained, and furthered my interest in and understanding of ceramics. In particular, I should like to mention Dr. J. E. Burke, whose parallel interests in physical ceramics have led to many fruitful discussions and new understanding, Professor F. H. Norton, who first introduced me to ceramics, and Professor John Chipman, who has provided advice, encouragement, and assistance at critical junctions.

W. D. KINGERY

Cambridge, Massachusetts
November 1960

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part I

INTRODUCTION

This book is primarily concerned with understanding the development, use, and control of the properties of ceramics from the point of view of what has become known as *physical ceramics.*

Until a decade or so ago, ceramics was in large part an empirical art. Users of ceramics procured their material from one supplier and one particular plant of a supplier in order to maintain uniformity (some still do). Ceramic producers were reluctant to change any detail of their processing and manufacturing (some still are). The reason was that the complex systems being used were not sufficiently well known to allow the effects of changes to be predicted or understood, and to a considerable extent this remains true. However, the fractional part of undirected empiricism in ceramic technology has greatly diminished.

Analysis of ceramics shows them to be a mixture of crystalline phases and glasses, each of many different compositions, usually combined with porosity, in a wide variety of proportions and arrangements. Experience has shown that focusing our attention on the structure of this assemblage in the broadest sense, from the viewpoint of both the origin of the structure and its influence on properties, is a powerful and effective approach. This concentration on the origin of structure and its influence on properties is the central concept of physical ceramics.

To be fully fruitful, structure must be understood in its most comprehensive sense. On one hand, we are concerned with atomic structure—the energy levels in atoms and ions that are so important in understanding the formation of compounds, the colors in glazes, the optical properties of lasers, electrical conductivity, magnetic effects, and a host of other characteristics of useful ceramics. Equally important is the way in which atoms or ions are arranged in crystalline solids and in noncrystalline glasses, from the point of view of not only lattices and ideal structures but

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also the randomness or ordering of the atoms and lattice defects such as vacant sites, interstitial atoms, and solid solutions. Properties such as heat conduction, optical properties, diffusion, mechanical deformation, cleavage, and dielectric and magnetic properties are influenced by these considerations. Departures from crystalline perfection at line imperfections called dislocations and at surfaces and interfaces also have a critical influence on many, perhaps most, properties of real systems.

At another level, the arrangement of phases—crystalline, glass, porosity—is often controlling, as is the nature of the boundaries between phases. A tenth of a percent porosity changes a ceramic from transparent to translucent. A change in pore morphology changes a ceramic from gastight to permeable. A decrease in grain size may change a ceramic from weak and friable to strong and tough. One refractory with crystal–crystal bonds and a large glass content withstands deformation at high temperature; another with a much smaller glass content penetrating between grains deforms readily. Changing the arrangement of phases can change an insulator into a conductor, and vice versa. The separation of a glass into two phases by appropriate heat treatment can dramatically alter many of its properties and increase or decrease its usefulness.

These observations are of academic interest, but even more they provide a key to the successful preparation and use of real ceramics. This approach provides us with the basis for understanding the source, composition, and arrangement of the phases that make up the final product; in addition, it provides the basis for understanding the resultant properties of a mixture of two or more phases. Such understanding must ultimately provide the basis for effective control and use; it is not only more satisfying intellectually but also more useful practically than the alternative—trying to learn by rote the characteristics of thousands of different materials. A further advantage of the method of this book is that it provides a single basis for understanding the preparation, properties, and uses of both new ceramics and traditional compositions.

1

Ceramic Processes and Products

We define ceramics as the art and science of making and using solid articles which have as their essential component, and are composed in large part of, inorganic nonmetallic materials. This definition includes not only materials such as pottery, porcelain, refractories, structural clay products, abrasives, porcelain enamels, cements, and glass but also nonmetallic magnetic materials, ferroelectrics, manufactured single crystals, glass-ceramics, and a variety of other products which were not in existence until a few years ago and many which do not exist today.

Our definition is broader than the art and science of making and using solid articles formed by the action of heat on earthy raw materials, an extension of the Greek word *keramos*, and is much broader than a common dictionary definition such as "pottery" or "earthenware." Modern developments in methods of fabrication, the use of materials to close specifications, and their new and unique properties make traditional definitions too restrictive for our purposes. The origination of novel ceramic materials and new methods of manufacture requires us to take a fundamental approach to the art and science and a broad view of the field.

1.1 The Ceramic Industry

The ceramic industry is one of the large industries of the United States, with an annual production of nearly $20 billion in 1974.

One important characteristic of the ceramic industry is that it is basic to the successful operation of many other industries. For example, refractories are a basic component of the metallurgical industry. Abrasives are essential to the machine-tool and automobile industries. Glass products are essential to the automobile industry as well as to the architectural, electronic, and electrical industries. Uranium oxide fuels are essential to the nuclear-power industry. Cements are essential to the architectural and

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inorganic nonmetallic crystalline solids formed by complex geologic processes. Their ceramic properties are largely determined by the crystal structure and the chemical composition of their essential constituents and the nature and amounts of accessory minerals present. The mineralogic characteristics of such materials and therefore their ceramic properties are subject to wide variation among different occurrences or even within the same occurrence, depending on the geological environment in which the mineral deposit was formed as well as the physical and chemical modifications that have taken place during subsequent geological history.

Since silicate and aluminum silicate materials are widely distributed, they are also inexpensive and thus provide the backbone of high-tonnage products of the ceramic industry and determine to a considerable extent its form. Low-grade clays are available almost everywhere; as a result, the manufacture of building brick and tile not requiring exceptional properties is a localized industry for which extensive beneficiation of the raw material is not appropriate. In contrast, for fine ceramics requiring the use of better-controlled raw materials, the raw materials are normally beneficiated by mechanical concentration, froth floatation, and other relatively inexpensive processes. For materials in which the value added during manufacture is high, such as magnetic ceramics, nuclear-fuel materials, electronic ceramics, and specialized refractories, chemical purification and even chemical preparation of raw materials may be necessary and appropriate.

The raw materials of widest application are the clay minerals—fine-particle hydrous aluminum silicates which develop plasticity when mixed with water. They vary over wide limits in chemical, mineralogical, and physical characteristics, but a common characteristic is their crystalline layer structure, consisting of electrically neutral aluminosilicate layers, which leads to a fine particle size and platelike morphology and allows the particles to move readily over one another, giving rise to physical properties such as softness, soapy feel, and easy cleavage. Clays perform two important functions in ceramic bodies. First, their characteristic plasticity is basic to many of the forming processes commonly used; the ability of clay–water compositions to be formed and to maintain their shape and strength during drying and firing is unique. Second, they fuse over a temperature range, depending on composition, in such a way as to become dense and strong without losing their shape at temperatures which can be economically attained.

The most common clay minerals and those of primary interest to ceramists, since they are the major component of high-grade clays, are based on the kaolinite structure, $Al_2(Si_2O_5)(OH)_4$. Other compositions often encountered are shown in Table 1.1.

Table 1.1. Ideal Chemical Formulas of the Clay Minerals

Kaolinite	$Al_2(Si_2O_5)(OH)_4$
Halloysite	$Al_2(Si_2O_5)(OH)_4 \cdot 2H_2O$
Pyrophyllite	$Al_2(Si_2O_5)_2(OH)_2$
Montmorillonite	$\left(Al_{1.67}\ {}^{Na_{0.33}}_{Mg_{0.33}}\right)(Si_2O_5)_2(OH)_2$
Mica	$Al_2K(Si_{1.5}Al_{0.5}O_5)_2(OH)_2$
Illite	$Al_{2-x}Mg_xK_{1-x-y}(Si_{1.6-y}Al_{0.6+y}O_5)_2(OH)_2$

A related material is talc, a hydrous magnesium silicate with a layer structure similar to the clay minerals and having the ideal formula $Mg_3(Si_2O_5)_2(OH)_2$. Talc is an important raw material for the manufacture of electrical and electronic components and for making tile. Asbestos minerals are a group of hydrous magnesium silicates which have a fibrous structure. The principal variety is chrysotile, $Mg_3Si_2O_5(OH)_4$.

In addition to the hydrous silicates already discussed, anhydrous silica and silicate materials are basic raw materials for much of the ceramic industry. SiO_2 is a major ingredient in glass, glazes, enamels, refractories, abrasives, and whiteware compositions. It is widely used because it is inexpensive, hard, chemically stable, and relatively infusable and has the ability to form glasses. There is a variety of mineral forms in which silica occurs, but by far the most important as a raw material is quartz. It is used as quartzite rock, as quartz sand, and as finely ground *potter's flint*. The major source of this material is sandstone, which consists of lightly bonded quartz grains. A denser quartzite, *gannister*, is used for refractory brick. Quartz is also used in the form of large, nearly perfect crystals, but these have been mostly supplanted by synthetic crystals, manufactured by a hydrothermal process.

Together with quartz, which serves as a refractory backbone constituent, and clay, which provides plasticity, traditional triaxial porcelains (originally invented in China) include feldspar, an anhydrous aluminosilicate containing K^+, Na^+, or Ca^{2+} as a flux which aids in the formation of a glass phase. The major materials of commercial interest are potash feldspar (microcline or orthoclase), $K(AlSi_3)O_8$, soda feldspar (albite), $Na(AlSi_3)O_8$, and lime feldspar (anorthite), $Ca(Al_2Si_2)O_8$. Other related materials sometimes used are nepheline syenite, a quartzfree igneous rock composed of nephelite, $Na_2(Al_2Si_2)O_8$, albite, and microcline; also wollastonite, $CaSiO_3$. One group of silicate minerals, the sillimanite group, having the composition Al_2SiO_5, is used for the manufacture of refractories.

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Most of the naturally occurring nonsilicate materials are used primarily as refractories. Aluminum oxide is mostly prepared from the mineral bauxite by the Bayer process, which involves the selective leaching of the alumina by caustic soda, followed by the precipitation of aluminum hydroxide. Some bauxite is used directly in the electric-furnace production of alumina, but most is first purified. Magnesium oxide is produced both from natural magnesite, $MgCO_3$, and from magnesium hydroxide, $Mg(OH)_2$, obtained from seawater or brines. Dolomite, a solid solution of calcium and magnesium carbonates with the formula $CaMg(CO_3)_2$, is used to make basic brick for use in the steel industry. Another refractory widely used for metallurgical purposes is chrome ore, which consists primarily of a complex solid solution of spinels, $(Mg,Fe)(Al,Cr)_2O_4$, which make up most of the material; the remainder consists of various magnesium silicates.

Other mineral-based materials which are widely used include soda ash, $NaCO_3$, mostly manufactured from sodium chloride; borate materials including kernite, $Na_2B_4O_7 \cdot 4H_2O$, and borax, $Na_2B_4O_7 \cdot 10H_2O$, used as fluxing agents; fluorspar, CaF_2, used as a powerful flux for some glazes and glasses; and phosphate materials mostly derived from apatite, $Ca_5(OH,F)(PO_4)_3$.

Although most traditional ceramic formulations are based on the use of natural mineral materials which are inexpensive and readily available, an increasing fraction of specialized ceramic ware depends on the availability of chemically processed materials which may or may not start directly from mined products and in which the particle-size characteristics and chemical purity are closely controlled. Silicon carbide for abrasives is manufactured by electrically heating mixtures of sand and coke to a temperature of about 2200°C where they react to form SiC and carbon monoxide. Already mentioned, seawater magnesia, Bayer alumina, and soda ash are widely used chemical products. In the manufacture of barium titanate capacitors, chemically purified titania and barium carbonate are used as raw materials. A wide range of magnetic ceramics is manufactured from chemically precipitated iron oxide. Nuclear-fuel elements are manufactured from chemically prepared UO_2. Single crystals of sapphire and ruby and also porefree polycrystalline aluminum oxide are prepared from aluminum oxide made by precipitating and carefully calcining alum in order to maintain good control of both chemistry and particle size. Special techniques of material preparation such as freeze-drying droplets of solution to form homogeneous particles of small size and high purity are receiving increasing attention, as is the vapor deposition of thin-film materials in a carefully controlled chemical and physical form. In general, raw-material preparation is clearly headed

toward the increasing use of mechanical, physical, and chemical purification and upgrading of raw materials together with special control of particle size and particle-size distribution and away from the sole reliance on materials in the form found in nature.

Forming and Firing. The most critical factors affecting forming and firing processes are the raw materials and their preparation. We have to be concerned with both the particle size and the particle-size distribution of the raw materials. Typical clay materials have a particle-size distribution which ranges from 0.1 to 50 microns for the individual particles. For the preparation of porcelain compositions the flint and feldspar constituents have a substantially larger particle size ranging between 10 and 200 microns. The fine-particle constituents, which for special ceramics may be less than 1 micron, are essential for the forming process, since colloidal suspensions, plastic mixes with a liquid-phase binder, and dry pressing all depend on very small particles flowing over one another or remaining in a stable suspension. For suspensions, the settling tendency is directly proportional to the density and particle size. For plastic forming the coherence of the mass and its yield point are determined by the capillarity of the liquid between particles; this force is inversely proportional to the particle size. However, if all the material were of a uniformly fine particle size, it would not be feasible to form a high concentration of solids. Mixing in a coarser material allows the fines to fill the interstices between the coarse particles such that a maximum particle-packing density is achieved at a ratio of about 70% coarse and 30% fine material when two particle sizes are used. In addition, during the drying process, shrinkage results from the removal of water films between particles. Since the number of films increases as the particle size decreases, bodies prepared with a liquid binder and all fine-particle materials have a high shrinkage during drying and the resultant problems of warping and distortion.

In addition to a desired particle size and particle-size distribution, intimate mixing of material is necessary for uniformity of properties within a body and for the reaction of individual constituents during the firing process. For preparing slurries or a fine-grain plastic mass, it is the usual practice to use wet mixing, with the raw materials placed together in ball mills or a blunger. Shearing stresses developed in the mixing process improve the properties of a plastic mix and ensure the uniform distribution of the fine-grain constituent. For dewatering the wet-milled mix, either a filter press may be used, or more commonly spray-drying, in which droplets of the slurry are dried with a countercurrent of warm air to maintain their uniform composition during drying. The resulting aggregates, normally 1 mm or so in size, flow and deform readily in subsequent forming.

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Since the firing process also depends on the capillary forces resulting from surface energy to consolidate and densify the material and since these forces are inversely proportional to particle size, a substantial percentage of fine-particle material is necessary for successful firing. The clay minerals are unique in that their fine particle size provides both the capability for plastic forming and also sufficiently large capillary forces for successful firing. Other raw materials have to be prepared by chemical precipitation or by milling into the micron particle range for equivalent results to be obtained.

Perhaps the simplest method of compacting a ceramic shape consists of forming a dry or slightly damp powder, usually with an organic binder, in a metal die at sufficiently high pressures to form a dense, strong piece. This method is used extensively for refractories, tiles, special electrical and magnetic ceramics, spark-plug insulators and other technical ceramics, nuclear-fuel pellets, and a variety of products for which large numbers of simple shapes are required. It is relatively inexpensive and can form shapes to close tolerances. Pressures in the range of 3000 to 30,000 psi are commonly used, the higher pressures for the harder materials such as pure oxides and carbides. Automatic dry pressing at high rates of speed has been developed to a high state of effectiveness. One limitation is that for a shape with a high length-to-diameter ratio the frictional forces of the powder, particularly against the die wall, lead to pressure gradients and a resulting variation of density within the piece. During firing these density variations are eliminated by material flow during sintering; it necessarily follows that there is a variation in shrinkage and a loss of the original tolerances. One modification of the dry-pressing method which leads to a more uniform density is to enclose the sample in a rubber mold inserted in a hydrostatic chamber to make pieces by hydrostatic molding, in which the pressure is more uniformly applied. Variations in sample density and shrinkage are less objectionable. This method is widely used for the manufacture of spark-plug insulators and for special electrical components in which a high degree of uniformity and high level of product quality are required.

A quite different method of forming is to extrude a stiff plastic mix through a die orifice, a method commonly used for brick, sewer pipe, hollow tile, technical ceramics, electrical insulators, and other materials having an axis normal to a fixed cross section. The most widely practiced method is to use a vacuum auger to eliminate air bubbles, thoroughly mix the body with 12 to 20% water, and force it through a hardened steel or carbide die. Hydraulic piston extruders are also widely used.

The earliest method of forming clay ware, one still widely used, is to add enough water so that the ware can readily be formed at low pressures.

This may be done under hand pressure such as building ware with coils, free-forming ware, or hand throwing on a potter's wheel. The process can be mechanized by soft-plastic pressing between porous plaster molds and also by automatic *jiggering*, which consists of placing a lump of soft plastic clay on the surface of a plaster-of-paris mold and rotating it at about 400 rpm while pulling a profile tool down on the surface to spread the clay and form the upper surface.

When a larger amount of water is added, the clay remains sticky plastic until a substantial amount has been added. Under a microscope it is seen that individual clay particles are gathered in aggregates or flocs. However, if a small quantity of sodium silicate is added to the system, there is a remarkable change, with a substantial increase in fluidity resulting from the individual particles being separated or *deflocculated.* With proper controls a fluid suspension can be formed with as little as 20% liquid, and a small change in the liquid content markedly affects the fluidity. When a suspension such as this is cast into a porous plaster-of-paris mold, the mold sucks liquid from the contact area, and a hard layer is built on the surface. This process can be continued until the entire interior of the mold is filled (solid casting) or the mold can be inverted and the excess liquid poured out after a suitable wall thickness is built up (drain casting).

In each of the processes which require the addition of some water content, the drying step in which the liquid is removed must be carefully controlled for satisfactory results, more so for the methods using a higher liquid content. During drying, the initial drying rate is independent of the water content, since in this period there is a continuous film of water at the surface. As the liquid evaporates, the particles become pressed more closely together and shrinkage occurs until they are in contact in a solid structure free from water film. During the shrinkage period, stresses, warping, and possibly cracks may develop because of local variations in the liquid content; during this period rates must be carefully controlled. Once the particles are in contact, drying can be continued at a more rapid rate without difficulty. For the dry-pressing or hydrostatic molding process, the difficulties associated with drying are avoided, an advantage for these methods.

After drying, ceramic ware is normally fired to temperatures ranging from 700 to 1800°C, depending on the composition and properties desired. Ware which is to be glazed or decorated may be fired in different ways. The most common procedure is to fire the ware without a glaze to a sufficiently high temperature to mature the body; then a glaze is applied and fired at a low temperature. Another method is to fire the ware initially to a low temperature, a bisque fire; then apply the glaze and mature the body and glaze together at a higher temperature. A third method is to

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apply the glaze to the unfired ware and heat them together in a one-fire process.

During the firing process, either a viscous liquid or sufficient atomic mobility in the solid is developed to permit chemical reactions, grain growth, and sintering; the last consists of allowing the forces of surface tension to consolidate the ware and reduce the porosity. The volume shrinkage which occurs is just equal to the porosity decrease and varies from a few to 30 or 40 vol%, depending on the forming process and the ultimate density of the fired ware. For some special applications, complete density and freedom from all porosity are required, but for other applications some residual porosity is desirable. If shrinkage proceeds at an uneven rate during firing or if part of the ware is restrained from shrinking by friction with the material on which it is set, stresses, warping, and cracking can develop. Consequently, care is required in setting the ware to avoid friction. The rate of temperature rise and the temperature uniformity must be controlled to avoid variations in porosity and shrinkage. The nature of the processes taking place is discussed in detail in Chapters 11 and 12.

Several different types of kilns are used for firing ware. The simplest is a skove kiln in which a benchwork of brick is set up inside a surface coating with combustion chambers under the material to be fired. Chamber kilns of either the up-draft or down-draft type are widely used for batch firing in which temperature control and uniformity need not be too precise. In order to achieve uniform temperatures and maximum use of fuel, chamber kilns in which the air for combustion is preheated by the cooling ware in an adjacent chamber, the method used in ancient China, is employed. The general availability of more precise temperature controls for gas, oil, and electric heating and the demands for ware uniformity have led to the increased use of tunnel kilns in which a temperature profile is maintained constant and the ware is pushed through the kiln to provide a precise firing schedule under conditions such that effective control can be obtained.

Melting and Solidification. For most ceramic materials the high volume change occurring during solidification, the low thermal conductivity, and the brittle nature of the solid phase have made melting and solidification processes comparable with metal casting and foundry practice inappropriate. Recently, techniques have been developed for unidirectional solidification in which many of these difficulties can be substantially avoided. This process has mainly been applied to forming controlled structures of metal alloys which are particularly attractive for applications such as turbine blades for high-temperature gas turbines. So far as we are aware, there is no large scale manufacture of ceramics in this way,

but we anticipate that the development of techniques for the unidirectional solidification of ceramics will be an area of active research during the next decade.

Another case in which these limitations do not apply is that of glass-forming materials in which the viscosity increases over a broad temperature range so that there is no sharp volume discontinuity during solidification and the forming processes can be adjusted to the fluidity of the glass. Glass products are formed in a high-temperature viscous state by five general methods: (1) blowing, (2) pressing, (3) drawing, (4) rolling, and (5) casting. The ability to use these processes depends to a large extent on the viscous flow characteristics of the glass and its dependence on temperature. Often surface chilling permits the formation of a stable shape while the interior remains sufficiently fluid to avoid the buildup of dangerous stresses. Stresses generated during cooling are relieved by annealing at temperatures at which the force of gravity is insufficient to cause deformation. This is usually done in an annealing oven or lehr which, for many silicate glasses, operates at temperatures in the range of 400 to 500°C.

The characteristics most impressive about commercial glass-forming operations are the rapidity of forming and the wide extent of automation. Indeed, this development is typical of the way in which technical progress affects an industry. Before the advent of glass-forming machinery, a major part of the container industry was based on ceramic stoneware. Large numbers of relatively small stoneware potters existed solely for the manufacture of containers. The development of automatic glass-forming machinery allowing the rapid and effective production of containers on a continuous basis has eliminated stoneware containers from common use.

Special Processes. In addition to the broadly applicable and widely used processes discussed thus far, there is a variety of special processes which augment, modify, extend, or replace these forming methods. These include the application of glazes, enamels, and coatings, hot-pressing materials with the combined application of pressure and temperature, methods of joining metals to ceramics, glass crystallization, finishing and machining operations, preparation of single crystals, and vapor-deposition processes.

Much ceramic ware is coated with a glaze, and porcelain enamels are commonly applied on a base of sheet steel or cast iron as well as for special jewelry applications. Glazes and enamels are normally prepared in a wet process by milling together the ingredients and then applying the coating by brushing, spraying, or dipping. For continuous operation, spray coating is most frequently used, but for some applications more satisfactory coverage can be obtained by dipping or painting. For

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porcelain enamels on cast iron, large castings heated in a furnace are coated with a dry enamel powder which must be distributed uniformly over the surface, where it fuses and sticks. In addition to these widely used processes, special coatings for technical ware have been applied by flame spraying to obtain a refractory dense layer; vacuum-deposited coatings have been formed by evaporation or cathodic sputtering; coatings have been applied by chemical vapor deposition; electrophoretic deposition has been applied; and other specialized techniques have had some limited applications.

To obtain a high density together with fine particle size, particularly for materials such as carbides and borides, the combination of pressure with high temperature is an effective technique mostly used for small samples of a simple configuration. At lower temperatures, glass-bonded mica is formed in this way for use as an inexpensive insulation. One of the main advantages of the hot-pressing method is that material preparation is less critical than for the sintering processes, which require a high degree of material uniformity for successful applications of the highest-quality products. The main difficulties with hot-pressing techniques are applying the method to large shapes and the time required for heating the mold and sample, which makes the method slow and expensive.

For many applications, joining processes are necessary to form fabricated units. In manufacturing teacups, for example, the handle is normally molded separately, dipped in a slip, and stuck on the body of the cup. Sanitary fixtures of complex design are similarly built up from separately formed parts. For many electronic applications requiring pressure-tight seals, it is necessary to form a bond between metals and ceramics. For glass-metal seals, the main problem is matching the expansion coefficient of the glass to that of the metal and designing the seal so that large stresses do not develop in use; special metal alloys and sealing glasses have been designed for this purpose. For crystalline ceramics, the most widely applied method has been to use a molybdenum-manganese layer which, when fired under partially oxidizing conditions, forms an oxide that reacts with the ceramic to give an adhesive bonding layer. In some cases, reactive metal brazes containing titanium or zirconium have been used.

One of the most important developments in ceramic forming has been to use a composition which can be formed as a glass and then transformed subsequent to forming into a product containing crystals of controlled size and amount. Classic examples of this are the striking gold-ruby glasses, in which the color results from the formation of colloidal gold particles. During rapid initial cooling, nucleation of the metal particles

occurs; subsequent reheating into the growth region develops proper crystallite sizes for the colloidal ruby color. In the past 10 years there has been extensive development of glasses in which the volume of crystals formed is much larger than the volume of the residual glass. By controlled nucleation and growth, glass-ceramics are made in which the advantage of automatic glass-forming processes is combined with some of the desirable properties of a highly crystalline body.

For most forming operations, some degree of finishing or machining is required which may range from fettling the mold lines from a slip-cast shape to diamond-grinding the final contour of a hard ceramic. For hard materials such as aluminum oxide, as much machining as feasible is done in the unfired state or the presintered state, with final finishing only done on the hard, dense ceramic where required.

A number of processes have been developed for the formation of ceramics directly from the vapor phase. Silica is formed by the oxidation of silicon tetrachloride. Boron and silicon carbide fibers are made by introducing a volatile chloride with a reducing agent into a hot zone, where deposition occurs on a fine tungsten filament. Pyrolytic graphite is prepared by the high-temperature deposition of graphite layers on a substrate surface by the pyrolytic decomposition of a carbon-containing gas. Many carbides, nitrides, and oxides have been formed by similar processes. For electronic applications, the development of single-crystal films by these techniques appears to have many potential applications.

Thin-wafer substrates are formed by several techniques, mostly from alumina. A widely used development is the technique in which a fluid body is prepared with an organic binder and uniformly spread on a moving nonporous belt by a doctor blade to form thin, tough films which can subsequently be cut to shape; holes can be introduced in a high-speed punch press.

There is an increasing number of applications in which it is necessary or desirable to have single-crystal ceramics because of special optical, electrical, magnetic, or strength requirements. The most widespread method of forming these is the Czochralski process, in which the crystal is slowly pulled from a molten melt, a process used for aluminum oxide, ruby, garnet, and other materials. In the Verneuil process a liquid cap is maintained on a growing boule by the constant-rate addition of powdered material at the liquid surface. For magnetic and optical applications thin single-crystal films are desirable which have been prepared by epitaxial growth from the vapor phase. Hydrothermal growth from solution is widely used for the preparation of quartz crystals, largely replacing the use of natural mineral crystals for device applications.

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1.3 Ceramic Products

The diversity of ceramic products, which range from microscopic single-crystal whiskers, tiny magnets, and substrate chips to multiton refractory furnace blocks, from single-phase closely controlled compositions to multiphase multicomponent brick, and from porefree transparent crystals and glasses to lightweight insulating foams is such that no simple classification is appropriate. From the point of view of historical development and tonnage produced, it is convenient to consider the mineral-raw-material products, mostly silicates, separately from newer nonsilicate formulations.

Traditional Ceramics. We can define traditional ceramics as those comprising the silicate industries—primarily clay products, cement, and silicate glasses.

The art of making pottery by forming and burning clay has been practiced from the earliest civilizations. Indeed, the examination of pottery fragments has been one of the best tools of the archeologist. Burnt clayware has been found dating from about 6500 B.C. and was well developed as a commercial product by about 4000 B.C.

Similarly, the manufacture of silicate glasses is an ancient art. Naturally occurring glasses (obsidian) were used during the Stone Age, and there was a stable industry in Egypt by about 1500 B.C.

In contrast, the manufacture of portland cement has only been practiced for about 100 years. The Romans combined burned lime with volcanic ash to make a natural hydraulic cement; the art seems then to have disappeared, but the hydraulic properties of lightly burned clayey limes were rediscovered in England about 1750, and in the next 100 years the manufacturing process, essentially the same as that used now, was developed.

By far the largest segment of the silicate ceramic industry is the manufacture of various glass products. These are manufactured mostly as sodium-calcium-silicate glasses. The next largest segment of the ceramic industry is lime and cement products. In this category the largest group of materials is hydraulic cements such as those used for building construction. A much more diverse group of products is included in the classification of whitewares. This group includes pottery, porcelain, and similar fine-grained porcelainlike compositions which comprise a wide variety of specific products and uses. The next classification of traditional ceramics is porcelain enamels, which are mainly silicate glasslike coatings on metals. Another distinct group is the structural clay products, which consist mainly of brick and tile but include a variety of similar products such as sewer pipe. A particularly important group of the traditional

ceramics industry is refractories. About 40% of the refractory industry consists of fired-clay products, and another 40% consists of heavy nonclay refractories such as magnesite, chromite, and similar compositions. In addition there is a sizable demand for various special refractory compositions. The abrasives industry produce mainly silicon carbide and aluminum oxide abrasives. Finally, a segment of the ceramic industry which does not produce ceramic products as such is concerned with the mineral preparation of ceramic and related raw materials.

Most of these traditional ceramics could be adequately defined as the silicate industries, which indeed was the description originally proposed for the American Ceramic Society in 1899. The silicate industries still compose by far the largest part of the whole ceramic industry, and from this point of view they can be considered the backbone of the field.

New Ceramics. In spite of its antiquity, the ceramic industry is not stagnant. Although traditional ceramics, or silicate ceramics, account for the large bulk of material produced, both in tonnage and in dollar volume, a variety of new ceramics has been developed in the last 20 years. These are of particular interest because they have either unique or outstanding properties. Either they have been developed in order to fulfill a particular need in greater temperature resistance, superior mechanical properties, special electrical properties, and greater chemical resistivity, or they have been discovered more or less accidentally and have become an important part of the industry. In order to indicate the active state of development, it may be helpful to describe briefly a few of these new ceramics.

Pure oxide ceramics have been developed to a high state of uniformity and with outstanding properties for use as special electrical and refractory components. The oxides most often used are alumina (Al_2O_3), zirconia (ZrO_2), thoria (ThO_2), beryllia (BeO), magnesia (MgO), spinel ($MgAl_2O_4$), and forsterite (Mg_2SiO_4).

Nuclear fuels based on uranium dioxide (UO_2) are widely used. This material has the unique ability to maintain its good properties after long use as a fuel material in nuclear reactors.

Electrooptic ceramics such as lithium niobate ($LiNbO_3$) and lanthanum-modified lead zirconate titanate (PLZT) provide a medium by which electrical information can be transformed to optical information or by which optical functions can be performed on command of an electrical signal.

Magnetic ceramics with a variety of compositions and uses have been developed. They form the basis of magnetic memory units in large computers. Their unique electrical properties are particularly useful in high-frequency microwave electronic applications.

Single crystals of a variety of materials are now being manufactured,

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either to replace natural crystals which are unavailable or for their own unique properties. Ruby and garnet laser crystals and sapphire tubes and substrates are grown from a melt; large quartz crystals are grown by a hydrothermal process.

Ceramic nitrides with unusually good properties for special applications have been developed. These include aluminum nitride, a laboratory refractory for melting aluminum; silicon nitrides and SiAlON, commercially important new refractories and potential gas turbine components; and boron nitride, which is useful as a refractory.

Enamels for aluminum have been developed and have become an important part of the architectural industry.

Metal-ceramic composites have been developed and are now an important part of the machine-tool industry and have important uses as refractories. The most important members of this group are various carbides bonded with metals and mixtures of a chromium alloy with aluminum oxide.

Ceramic carbides with unique properties have been developed. Silicon carbide and boron carbide in particular are important as abrasive materials.

Ceramic borides have been developed which have unique properties of high-temperature strength and oxidation resistance.

Ferroelectric ceramics such as barium titanate have been developed which have extremely high dielectric constants and are particularly important as electronic components.

Nonsilicate glasses have been developed and are particularly useful for infrared transmission, special optical properties, and semiconducting devices.

Molecular sieves which are similar to, but are more controlled than, natural zeolite compositions are being made with controlled structures so that the lattice spacing, which is quite large in these compounds, can be used as a means of separating compounds of different molecular sizes.

Glass-ceramics are a whole new family of materials based on fabricating ceramics by forming as a glass and then nucleating and crystallizing to form a highly crystalline ceramic material. Since the original introduction of Pyroceram by the Corning Glass Works the concept has been extended to dozens of compositions and applications.

Porefree polycrystalline oxides have been made based on alumina, yttria, spinel, magnesia, ferrites, and other compositions.

Literally dozens of other new ceramic materials unknown 10 or 20 years ago are now being manufactured and used. From this point of view the ceramic industry is one of our most rapidly changing industries, with new products having new and useful properties constantly being developed. These ceramics are being developed because there is a real need for new materials to transform presently available designs into practical, serviceable products. By far the major hindrance to the development of many new technologically feasible structures and systems is the lack of satisfactory materials. New ceramics are constantly filling this need.

New Uses for Ceramics. In the same way that the demand for new and better properties has led to the development of new materials, the availability of new materials had led to new uses based on their unique properties. This cycle of new ceramics–new uses–new ceramics has accelerated with the attainment of a better understanding of ceramics and their properties.

One example of the development of new uses for ceramics has occurred in the field of magnetic ceramic materials. These materials have hysteresis loops which are typical for ferromagnetic materials. Some have very nearly the square loop that is most desirable for electronic computer memory circuits. This new use for ceramics has led to extensive studies and development of materials and processes.

Another example is the development of nuclear power, which requires uranium-containing fuels having large fractions of uranium (or sometimes thorium), stability against corrosion, and the ability to withstand the fissioning of a large part of the uranium atoms without deterioration. For many applications UO_2 is an outstanding material for this fuel. Urania ceramics have become an important part of reactor technology.

In rocketry and missile development two critical parts which must withstand extreme temperatures and have good erosion resistance are the nose cone and the rocket throat. Ceramic materials are used for both.

For machining metals at high speeds it has long been known that oxide ceramics are superior in many respects as cutting tools. However, their relatively low and irregular strength makes their regular use impossible. The development of alumina ceramics with high and uniform strength levels has made them practicable for machining metals and has opened up a new field for ceramics.

In 1946 it was discovered that barium titanate had a dielectric constant 100 times larger than that of other insulators. A whole new group of these ferroelectric materials has since been discovered. They allow the manufacture of capacitors which are smaller in size but have a larger capacity than other constructions, thus improving electronic circuitry and developing a new use for ceramic materials.

In jet aircraft and other applications metal parts have had to be formed from expensive, and in wartime unobtainable, alloys to withstand the moderately high temperatures encountered. When a protective ceramic coating is applied, the temperature limit is increased, and either higher

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temperatures can be reached or less expensive and less critical alloys can be substituted.

Many further applications of ceramics which did not even exist a few years ago can be cited, and we may expect new uses to develop that we cannot now anticipate.

Suggested Reading

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part II

CHARACTERISTICS OF CERAMIC SOLIDS

The ceramic materials with which we are concerned may be single crystals, wholly vitreous, or mixtures of two or more crystalline or vitreous phases. Pore spaces are also a principal phase in most ceramic materials. As the basis for understanding the properties of real ceramics, it is essential to have an understanding of the properties of single crystals and noncrystalline solids. In Part II we consider the properties of ceramic solids as a single phase without regard to their source or the effects of combining with other materials.

In Chapter 2 we consider the structure of crystalline ceramics. The nature of the atomic arrangements, the forces between atoms, and the location of atoms in a crystalline lattice are important parameters basic to the properties of the crystal. In Chapter 3 we consider noncrystalline solids. The atomic structure of these materials is quite different from that of crystals, and many of their properties are intimately related to the noncrystalline nature of the atomic arrangement.

Both crystalline and noncrystalline materials depart from ideal structures in many respects. Some of their properties are strongly dependent on the nature of departures from perfect crystallinity or perfect randomness. Consequently, in Chapter 4 we consider structural imperfections, their source, and properties. In Chapter 5 we consider the surfaces and interfaces as a separate characteristic property. Finally, in Chapter 6 we consider the question of atomic mobility; this is important to many properties and is intimately related to the structure of solids. An understanding of these five chapters is essential to understanding the properties of more complex ceramics.

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In describing the characteristics of ceramic solids, two different points of view have been useful. One is to consider them from an atomistic point of view, defining as closely as possible the location of atoms relative to one another, the interaction between atoms, the motion of atoms relative to one another, and the influence of changed conditions, such as increased temperature, on atomic behavior. This point of view leads to an understanding of structure and an insight into atomic interaction that is essential for developing models and generalizations about the complex phenomena we wish to understand. It is an approach that first became practical about 60 years ago with the discovery of X-ray diffraction by crystals and has continued to depend strongly on observations of the interaction between radiation and matter.

A second and equally useful viewpoint is to consider the macroscopic properties of matter independent of conjectures about the details of atomic characteristics and interaction. This, the thermodynamic approach, depends on the observation that the state of matter at equilibrium, whether gaseous, liquid or crystalline, is determined by the thermodynamic variables which describe the system (temperature, volume, pressure, composition). The interrelationship of these variables to the state of the system has been formally developed in the principles of thermodynamics, which are based on three fundamental laws. The first law requires that the internal energy E of a system be conserved. The second law introduces another function, the entropy S, a measure of randomness which determines the direction of all spontaneous processes: the entropy of the world tends toward a maximum. Thus the change in the entropy of the system and the surroundings during any process is always toward greater randomness:

$$dS_{\text{system}} + dS_{\text{surroundings}} \geq 0 \tag{1}$$

At equilibrium, the entropy change is zero, and therefore this equation serves as a definition of thermodynamic equilibrium. The third law sets the zero-point entropy of matter at the absolute zero of temperature: the entropy of a perfect crystal at 0°K is zero.

From these three fundamental laws and from the definition of internal energy and entropy other useful state functions are defined: the enthalpy, or heat content H, the Gibbs free energy G, and the Helmholtz free energy F. The Gibbs free energy ($G = E + PV - TS = H - TS$) is the state function most commonly used to describe the equilibrium state of the system. For example, at equilibrium (0°C and 1 atm pressure), ice and water can coexist, and the free energy of water is equal to that of ice. From experience, we know that there is an enthalpy change, the heat of fusion, and also an entropy change associated with this equilibrium

reaction:

$$\Delta G = 0 = \Delta H - T_e\,\Delta S \tag{2}$$

$$\Delta S_{\text{ice to water}} = \frac{\Delta H_{\text{fusion}}}{T_e(273°\text{K})} \tag{3}$$

When we deal with phases of variable-composition (gaseous, liquid or solid solutions), the Gibbs free energy is not only a function of temperature and pressure but also of composition. If X_i is the mole fraction of the ith component,

$$dG = -S\,dT + V\,dP + \sum_i \mu_i\,dX_i \tag{4}$$

where we define the chemical potential μ_i as the change in the free energy of the system with respect to a change in the concentration of the ith component at constant temperature and pressure:

$$\mu_i = \left(\frac{\partial G}{\partial X_i}\right)_{T,P,X_{j\neq i}} \tag{5}$$

If the system is at equilibrium, each of the terms in Eq. 4 must be independent of time and of position in the system, that is, uniform temperature (thermal equilibrium), uniform pressure (mechanical equilibrium), and uniform chemical potential of each component (chemical equilibrium). In a multiphase system, this means that the chemical potential of a particular component must be the same in each phase.

As we proceed, it will become increasingly clear that the energy-matter relationships both on an atomistic scale and on a scale of macroscopic assemblages are areas of knowledge directly pertinent to ceramics. Many excellent texts are available; particularly recommended C. Kittel, *Introduction to Solid State Physics*, and R. A. Swalin, *Thermodynamics of Solids*.

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EXHIBIT PPP

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Definition of 'ceramic'

ceramic

Word Frequency ○○○○○

(sɪræmɪk)
Word forms: ceramics plural

1. **MASS NOUN**

Ceramic is clay that has been heated to a very high temperature so that it becomes hard.

...ceramic tiles.

2. **COUNTABLE NOUN** [usu pl]

Ceramics are ceramic ornaments or objects.

...a collection of Chinese ceramics.

3. **UNCOUNTABLE NOUN**

Ceramics is the art of making artistic objects out of clay.

...a degree in ceramics.

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ceramic 1 of 2 adjective

ce·ram·ic sə-ˈra-mik *especially British* kə-

: of or relating to the manufacture of any product (such as earthenware, porcelain, or brick) made essentially from a nonmetallic mineral (such as clay) by firing at a high temperature

also **:** of or relating to such a product

ceramic 2 of 2 noun

1 **ceramics** **plural in form but singular in construction** **:** the art or process of making ceramic articles

2 **:** a product of ceramic manufacture

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EXHIBIT RRR

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PHOTONICS MEDIA photonics.com

.: transparent

Capable of transmitting light with little absorption and no appreciable scattering or diffusion.

See Also

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"Nonlocal" Metasurface Enables High-Performing AR Eyeglasses	Photonics Spectra Dec 2022
Transparent Chip Provides View to Multimodal Imaging	BioPhotonics May/Jun 2022
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EXHIBIT SSS

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translucent

Pertaining to materials having the property of reflecting a part and transmitting a part of the incident radiation.

See Also

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Machine-Readable Labels Identify and Track Objects	Photonics.com Feb 2022

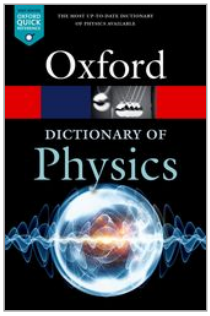
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A Dictionary of Physics (8 ed.)
Edited by: Richard Rennie and Jonathan Law

Publisher: Oxford University Press
Print ISBN-13: 9780198821472
Current Online Version: 2019
Print Publication Date: 2019
Published online: 2019
eISBN: 9780191860805

translucent

Permitting the passage of radiation but not without some scattering or diffusion. For example, frosted glass allows light to pass through it but an object cannot be seen clearly through it because the light rays are scattered by it. *Compare* TRANSPARENT.

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EXHIBIT UUU

semitransparent

adjective

Definition of *semitransparent* next

as in *translucent*

Synonyms & Similar Words

Relevance

translucent

diaphanous

colorless

sheer

lucid

semitranslucent

uncolored

transparentized

transparent

crystalline

liquid

crystal

pellucid

limpid

lucent

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crystal clear

see-through

clear

Antonyms & Near Antonyms

opaque

colored

cloudy

dark

tinted

glazed

smoky

hazy

misty

dense

nebulous

foggy

turbid

muddy

filmy

murky

smokey

See Less

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Thesaurus Entries Near *semitransparent*

semitranslucent
semitransparent
semitropical

See More Nearby Entries

Cite this Entry

Style

MLA

"Semitransparent." *Merriam-Webster.com Thesaurus*, Merriam-Webster, https://www.merriam-webster.com/thesaurus/semitransparent. Accessed 6 Aug. 2023.

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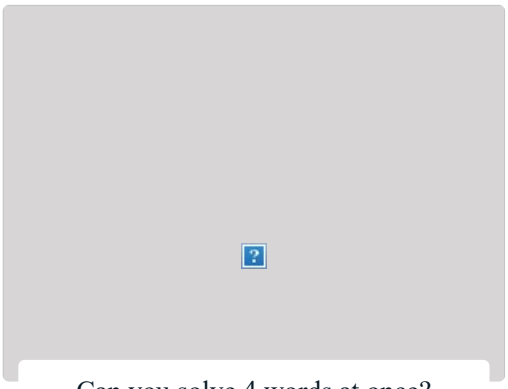
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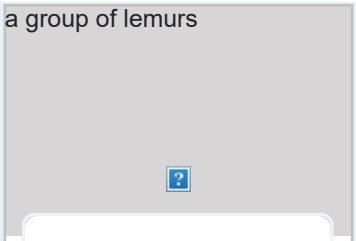
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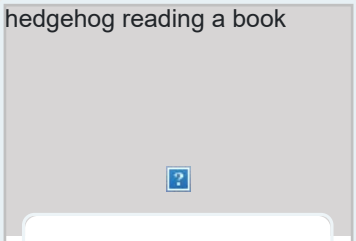
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Can you tell a meerkat from a wombat?

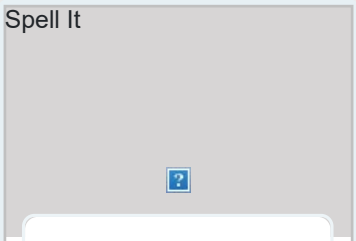
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EXHIBIT VVV

opaque

A term describing a substance that is impervious to light; the characteristic of a substance that has no luminous transmittance.

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EXHIBIT WWW

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maintain verb

main·tain mān-ˈtān mən-

maintained; maintaining; maintains

Synonyms of *maintain*

transitive verb

1 : to keep in an existing state (as of repair, efficiency, or validity) : preserve from failure or decline
maintain machinery

2 : to sustain against opposition or danger : uphold and defend
maintain a position

3 : to continue or persevere in : **CARRY ON**, **KEEP UP**
couldn't *maintain* his composure

4 a : to support or provide for
has a family to *maintain*

b : **SUSTAIN**
enough food to *maintain* life

5 : to affirm in or as if in argument : **ASSERT**
maintained that the earth is flat

mān-ˌtā-nə-ˈbi-lə-tē **noun**

mān-ˈtā-nə-bəl **adjective**

noun

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EXHIBIT XXX

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INTERNATIONAL STANDARD

ISO/IEC 18092

Second edition
2013-03-15

Information technology — Telecommunications and information exchange between systems — Near Field Communication — Interface and Protocol (NFCIP-1)

Technologies de l'information — Télécommunications et échange d'information entre systèmes — Communication de champ proche — Interface et protocole (NFCIP-1)

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of the joint technical committee is to prepare International Standards. Draft International Standards adopted by the joint technical committee are circulated to national bodies for voting. Publication as an International Standard requires approval by at least 75 % of the national bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO and IEC shall not be held responsible for identifying any or all such patent rights.

ISO/IEC 18092 was prepared by Joint Technical Committee ISO/IEC JTC 1, *Information technology*, Subcommittee SC 6, *Telecommunications and information exchange between systems*.

This second edition cancels and replaces the first edition (ISO/IEC 18092:2004), which has been technically revised.

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Introduction

This International Standard specifies the interface and protocol for simple wireless communication between close coupled devices. These Near Field Communication (NFC) devices communicate with bit rates of 106, 212, and 424 kbit/s.

This NFC Interface and Protocol (NFCIP-1) standard allows, but does not specify, applications in network products and consumer equipment.

The first edition of ISO/IEC 18092:2004 was prepared by Ecma International (as ECMA-340) and was adopted, under a special "fast-track procedure", by Joint Technical Committee ISO/IEC JTC 1, *Information technology*, in parallel with its approval by national bodies of ISO and IEC. This second edition of ISO/IEC 18092 was maintained by JTC 1/SC 6 and Ecma International; it cancels and replaces the first edition (ISO/IEC 18092:2004), which has been technically revised with fully backward compatibility.

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Information technology — Telecommunications and information exchange between systems — Near Field Communication — Interface and Protocol (NFCIP-1)

1 Scope

This International Standard defines communication modes for Near Field Communication Interface and Protocol (NFCIP-1) using inductive coupled devices operating at the centre frequency of 13,56 MHz for interconnection of computer peripherals. It also defines both the Active and the Passive communication modes of Near Field Communication Interface and Protocol (NFCIP-1) to realize a communication network using Near Field Communication devices for networked products and also for consumer equipment. This International Standard specifies, in particular, modulation schemes, codings, transfer speeds, and frame format of the RF interface, as well as initialisation schemes and conditions required for data collision control during initialisation. Furthermore, this International Standard defines a transport protocol including protocol activation and data exchange methods.

Information interchange between systems also requires, at a minimum, agreement between the interchange parties upon the interchange codes and the data structure.

2 Conformance

A system implementing the Active and the Passive communication mode shall be in conformance with this International Standard if it meets all the mandatory requirements specified herein.

It may also implement the NFC-SEC Option as specified in ISO/IEC 13157-1.

3 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ITU-T V.41:1988, *Code-independent error-control system*

ISO/IEC 13157-1:2010, *Information technology — Telecommunications and information exchange between systems — NFC Security — Part 1: NFC-SEC NFCIP-1 security services and protocol*

ISO/IEC 14443-2:2010, *Identification cards — Contactless integrated circuit cards — Proximity cards — Part 2: Radio frequency power and signal interface*

ISO/IEC 14443-3:2011, *Identification cards — Contactless integrated circuit cards — Proximity cards — Part 3: Initialization and anticollision*

ISO/IEC 14443-4:2008, *Identification cards — Contactless integrated circuit cards — Proximity cards — Part 4: Transmission protocol*

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4 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

4.1
active communication mode
mode in which both the Initiator and the Target use their own RF field to enable the communication

4.2
ASK modulation
Amplitude Shift Keying, in which the amplitude of the carrier frequency is modulated according to the logic of the data to be transmitted

4.3
Binary Coded Decimal
BCD
system for representing each of the decimal numbers 0 to 9 by a four-bit binary code

NOTE The bits, from left to right, are worth 8, 4, 2 and 1 respectively in decimal, so for example the number 6 in BCD is 0110.

4.4
collision
transmission by two or more Targets or Initiators during the same time period, such that the Initiator or the Target is unable to distinguish from which Target the data originated

4.5
frame
sequence of data bits and optional error detection bits, with frame delimiters at start and end

4.6
$H_{Threshold}$
the threshold value to detect an external RF field

4.7
Initiator
generator of the RF field and starter of the NFCIP-1 communication

4.8
load modulation
process of amplitude modulating a radio frequency field by varying the properties of a resonant circuit placed within the radio frequency field

4.9
lsb first
least significant bit first, indicating a serial data transmission system that sends lsb before all other bits

4.10
LSB first
Least Significant Byte first, indicating a serial data transmission system that sends LSB before all other bytes

4.11
Manchester coding
method of bit coding whereby a logic level during a bit duration is represented by a sequence of two defined physical states of a communication medium

4.12
modulation index
signal amplitude ratio of [*peak – minimum]* / [*peak + minimum*]

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4.13
msb first
most significant bit indicating a serial data transmission system that sends the msb before all other bits

4.14
MSB first
Most Significant Byte indicating a serial data transmission system that sends the MSB before all other bytes

4.15
NFCIP-1 device
entity [ISO/IEC 18092]

4.16
NFC Identifier
NFCIDn
a randomly generated number used by the RF Collision Avoidance and Single Device Detection sequence for both the Active and the Passive communication modes

4.17
NFC-SEC
NFCIP-1 Security Services and Protocol as specified in ISO/IEC 13157-1

4.18
passive communication mode
when the Initiator is generating the RF field and the Target responds to an Initiator command in a load modulation scheme

4.19
RF Collision Avoidance
RFCA
method to detect the presence of a RF field based on the carrier frequency and method to detect and resolve collisions on protocol level

4.20
SAK
Select acknowledge [ISO/IEC 14443-3]

NOTE SAK replaces the SEL_RES [ISO/IEC 18092:2004].

4.21
sensing
NFCIP-1 device in the Active communication mode expecting a Response to a Request it has sent on the RF field to detect the start of communication to receive the Request

4.22
Single Device Detection
SDD
algorithm used by the Initiator to detect one out of several Targets in its RF field (anti-collision [ISO/IEC 14443-3])

4.23
Target
responds to Initiator command either using load modulation scheme (RF field generated by Initiator) or using modulation of self generated RF field

4.24
Time Period
defines the number of slots used for RF Collision Avoidance

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4.25
Time Slot
method of preparing a time window when a Target answers, and assigning and identifying two or more logic channels

4.26
transaction
initialisation, data exchange and device de-selection

5 Conventions and notations

5.1 Representation of numbers

The following conventions and notations apply in this document unless otherwise stated.

— Letters and digits in single quotation mark represent numbers in hexadecimal notation.

— The setting of bits is denoted by ZERO or ONE.

— Numbers in binary notation and bit patterns are represented by strings of digits 0 and 1 shown with the most significant bit to the left. Within such strings, X may be used to indicate that the setting of a bit is not specified within the string. For example (XXXX)b.

5.2 Names

The names of basic elements, e.g. specific fields, are written with a capital initial letter.

6 Abbreviated terms

ALL_REQ	Wake up ALL Request
ATR	Attribute Request and Attribute Response
ATR_REQ	Attribute Request
ATR_RES	Attribute Response
BCD	Binary Code Decimal
BRi	Receiving bit duration supported by Initiator
BRt	Receiving bit duration supported by Target
BSi	Sending bit duration supported by Initiator
BSt	Sending bit duration supported by Target
CMD	Command
CRC	Cyclic Redundancy Check
D	Divisor
DEP	Data Exchange Protocol Request and Data Exchange Protocol Response
DEP_REQ	Data Exchange Protocol Request
DEP_RES	Data Exchange Protocol Response
DIDi	Initiator Device ID
DIDt	Target Device ID
DRi	Data rate Received by Initiator
DRt	Data rate Received by Initiator
DSi	Data rate Send by Initiator
DSL	Deselect Request and Deselect Response
DSL_REQ	Deselect Request
DSL_RES	Deselect Response
DSt	Data rate Send by Target
etu	elementary time unit
fc	Frequency of operating field (carrier frequency)
fd	Baseband frequency of Manchester coding

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fs [ISO/IEC 14443-2]	Subcarrier
FRT	Frame Response Time
Gi	Optional information field for Initiator
Gt	Optional information field for Target
HLTA [ISO/IEC 14443-3]	HaLT command, Type A
ID	Identification number
lsb	least significant bit
LSB	Least Significant Byte
MI	Multiple Information link for Data Exchange Protocol
msb	most significant bit
MSB	Most Significant Byte
NAD	Node Address
NFCID1	*fc*/128 UID
nfcid1*n*	Byte number *n* of NFCID1
NFCID2	Random ID for SDD in Passive communication mode at *fc*/64 and *fc*/32 bit rates
nfcid2*n*	Byte number n of the Random Identifier NFCID2
NFCID3	Random ID for transport protocol activation
nfcid3*n*	Byte number n of the Random Identifier NFCID3
P	Odd parity bit
PA	Preamble
PCD	Proximity Coupling Device [ISO/IEC 14443-2]
pdu	protocol data unit
PFB	Control information for transaction
PICC	Proximity Card or object [ISO/IEC 14443-2]
PNI	Packet Number Information
PPi	Protocol Parameters used by Initiator
PPt	Protocol Parameters used by Target
PSL	Parameter Selection Request and Parameter Selection Response
PSL_REQ	Parameter Selection Request
PSL_RES	Parameter Selection Response
RF	Radio Frequency
RFCA	RF Collision Avoidance
RFU	Reserved for Future Use
RLS	Release Request and Release Response
RLS_REQ	Release Request
RLS_RES	Release Response
RWT	Response Waiting Time
SB	Start byte for data exchange protocol at *fc*/128
SDD	Single Device Detection (anti-collision)
SEL_CMD	Select Command byte
SYNC	Synchronisation pattern
TO	Timeout value
UID	Unique Identifier [ISO/IEC 14443-3]
WT	Waiting Time
WUP	Wakeup Request and Wakeup Response
WUP_REQ	Wakeup Request
WUP_RES	Wakeup Response

7 General

NFCIP-1 Targets and Initiators shall implement both the Active and the Passive communication modes.

In the Active communication mode, both the Initiator and the Target use their own RF field to communicate. The Initiator starts the NFCIP-1 transaction. The Target responds to an Initiator command in the Active communication mode by modulating its own RF field.

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In the Passive communication mode, the Initiator generates the RF field and starts the transaction. The Target responds to an Initiator command in the Passive communication mode by modulating the Initiators' RF field which is referred to as load modulation.

This International Standard specifies requirements for modulation, bit rates and bit coding. In addition it specifies requirements for the start of communication, the end of communication, the bit and byte representation, the framing and error detection, the single device detection, the protocol and parameter selection and the data exchange and de-selection of Near Field Communication Interface and Protocol (NFCIP-1) devices.

Transactions start with device initialisation and end with device de-selection. Initiators and Targets exchange commands, responses and data in alternating or half duplex communication.

NFCIP-1 devices are capable to start transactions at bit rates of *fc*/128, *fc*/64 and *fc*/32. Initiators select one of those bit rates to start a transaction and they may change the bit rate using PSL_REQ/PSL_RES commands during a transaction.

The mode (Active or Passive) shall not be changed during one transaction.

8 RF field

8.1 Values

fc is 13,56 MHz.

H_{min} is 1,5 A/m (rms).

H_{max} is 7,5 A/m (rms).

$H_{Threshold}$ is 0,1875 A/m (rms).

8.2 Passive communication Mode

The Initiator shall generate field strength of at least H_{min} and not exceeding H_{max} at manufacturer specified positions (i.e. operating volume) under un-modulated conditions.

The Target shall operate continuously between H_{min} and H_{max}.

8.3 Active communication Mode

An Initiator and a Target shall alternately generate a RF field of at least H_{min} and not exceeding H_{max} at manufacturer specified positions (i.e. operating volume) under un-modulated conditions.

8.4 External RF field detection

NFCIP-1 devices shall detect external RF fields at *fc* with field strength higher than $H_{Threshold}$.

9 RF Signal Interface

9.1 Bit duration

One *etu* equals 128/(D × *fc*), where the values of the divisor D depend on the bit rate and communication mode, see Table 1.

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Table 1 — Divisor D

Communication Mode	bit rate	Divisor D
active or passive	*fc*/128 (~106 kbit/s)	1
active or passive	*fc*/64 (~212 kbit/s)	2
active or passive	*fc*/32 (~424 kbit/s)	4
Active	*fc*/16 (~848 kbit/s)	8
Active	*fc*/8 (~1695 kbit/s)	16
Active	*fc*/4 (~3390 kbit/s)	32
Active	*fc*/2 (~6780 kbit/s)	64

NOTE 1 The Initiator selects the communication mode (either Active or Passive) and bit rate (*fc*/128, *fc*/64 or *fc*/32 specified by the following clauses).

NOTE 2 This Standard does not specify the modulation and the bit coding beyond the bit rate of *fc*/32.

9.2 Active communication mode

Targets and Initiators shall comply with the following specifications for both communication directions, i.e. Initiator to Target and Target to Initiator.

9.2.1 Requirements for *fc*/128

9.2.1.1 Bit rate

The bit rate for the transmission during initialisation and single device detection shall be *fc*/128.

9.2.1.2 Modulation

See 8.1.2.1 of ISO/IEC 14443-2. During transmission, both the Initiator and the Target shall conform to PCD values. During reception, both the Initiator and the Target shall conform to PICC values.

9.2.1.3 Bit representation and coding

See 8.1.3 of the ISO/IEC 14443-2 for a bit rate of *fc*/128.

9.2.1.4 Byte transmission

Initiators and targets shall transmit bytes with the lsb first.

9.2.2 Requirements for *fc*/64 and *fc*/32

9.2.2.1 Bit rates

The bit rates for the transmission during initialisation and single device detection shall respectively be *fc*/64 or *fc*/32.

9.2.2.2 Modulation

See 9.1.2 of ISO/IEC 14443-2 for the bit rate of *fc*/64 and *fc*/32. During transmission, both the Initiator and the Target shall apply the PCD values. During reception, both the Initiator and the Target shall apply the PICC values.

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