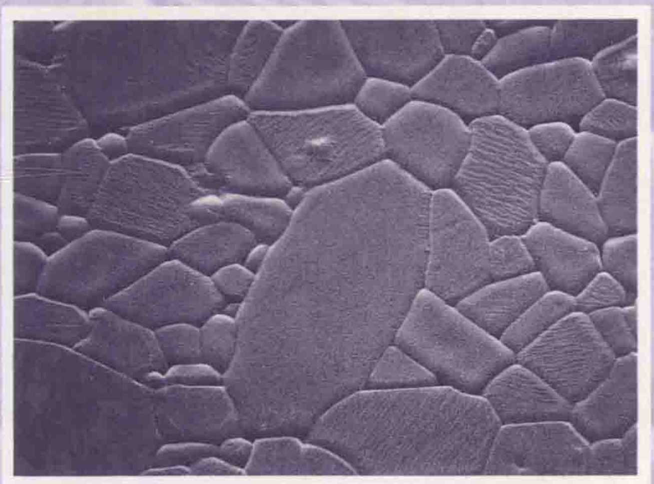
Corrosion Resistance of Technical Ceramics



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National Physical Laboratory

SECOND EDITION

NATIONAL PHYSICAL LABORATORY

Corrosion Resistance of Technical Ceramics

SECOND EDITION

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LONDON: HMSO

First Edition published 1983
Second Edition published 1991

ISBN 0 11 480060 X

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

HMSO

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CORROSION RESISTANCE OF TECHNICAL CERAMICS

SECOND EDITION

Preface
To the First Edition

Information about the behaviour of materials is of crucial importance to engineers. In the development of modern industry and technology, there is an urgent need to improve the quality, reliability and performance of engineering components, especially those used under severe conditions. In order to make technical progress it is necessary to develop new materials with improved special characteristics and properties, but it is equally important that each material should be chosen carefully, to ensure that it has the characteristics demanded by the application. This can best be accomplished if the selection is based on reliable data, and a sound scientific appreciation of the properties of materials. In the field of 'engineering' ceramics, there is a need for impartial comparative information to help designers in their selection and proper use. This need was perceived by two of my colleagues at the NPL, Drs T I Barry and R Morrell, who were largely responsible for formulating a research programme which had the purpose of providing data handbooks of critically appraised physical and chemical properties; this book is a product of that programme.

I must also acknowledge the other important contributions made by my colleagues. I thank Dr Morrell for providing much of the information, and for many valuable comments and discussions; Mr D J Clinton for supplying the excellent micrographs; and Mr A Grandjean for carrying out most of the photographic work. I am very grateful to Mr G O Lloyd and Drs Barry, Morrell and J A Champion, who read the draft manuscript, pointed out a number of errors and weaknesses, and made many helpful criticisms and suggestions. I also thank the UK suppliers of technical ceramics for providing detailed information about their products, and for useful guidance concerning the testing and use of the materials in corrosive environments.

L A LAY

Preface
To the Second Edition

During the years that have passed since the first edition was published, a number of new types of ceramic have been developed, and others have been significantly improved and become more widely available; these include the tough zirconia ceramics, alumina bioceramic, aluminium titanate, aluminium nitride, boron carbide, titanium diboride, and sintered silicon nitrides and silicon carbides. There has been a growing trend towards the use of high-purity powders for the production of both oxide and non-oxide ceramics, and this has commonly resulted in greatly improved corrosion resistance. The increasing number of published papers and reports dealing with the corrosion of ceramics demonstrates that interest in the subject is now much stronger. This revised and expanded edition aims to incorporate information about recent research and the newer ceramics to give a broader and more up-to-date coverage of the subject.

I would like to thank Barbara Sanger for carrying out the literature searches which enabled relevant papers and reports to be found, Diane Vincent and Drs T I Barry, J A Champion, R Morrell and M J Reece for reading the first draft and making many valuable criticisms and suggestions, and Kit Myer for her unlimited patience and helpfulness in preparing the typescript.

L A LAY

List of the classes of technical ceramics included

1. Silicates, porcelains, glass-ceramics.
2. Oxides, single and mixed
   BeO, MgO, $MgAl_2O_4$, Al_2O_3, Al_2TiO_5, TiO_2, Cr_2O_3, ZrO_2, SnO_2, ThO_2.
3. Carbides
   SiC, B_4C, TiC, ZrC, WC.
4. Nitrides
   Si_3N_4, Si-Al-O-N, BN, AlN, TiN.
5. Borides
   TiB_2, ZrB_2.
6. Silicides
   $MoSi_2$.
7. Sulphides
   CeS.
8. Carbons and graphites
   Industrial graphites, pyrolytic graphite, vitreous carbon.

Contents

CHAPTER 1

Introduction

1.1 The need for information about the corrosion resistance of ceramics

One of the outstanding advantages which ceramics have over other classes of material is their high level of chemical inertness in corrosive environments. This property is especially valuable at high temperatures, where plastics are unusable, and the performance of metals and alloys tends to become unsatisfactory due to softening or corrosion. In many cases, the only possible way of finding a solution to a materials problem is by using a ceramic. Of course, when a material is being sought, it is normally necessary for it to have some other property or combination of properties in addition to chemical inertness; frequently the use of a ceramic is determined by favourable thermal, mechanical, thermomechanical or wear resisting properties.

The use of cheap clay-based ceramics is well established in the chemical and associated industries for handling reactive substances. High-alumina ceramics have been developed for equipment such as pumps and valves for controlling acids, where clay-based materials are inadequate due to insufficient strength, hardness and wear resistance; strong impermeable grades of silicon carbide are even more durable in these applications. Many ceramics have excellent resistance to hot metals, and find uses such as components for controlling, metering and filtering molten metals, as dies for extrusion and as cutting tools.

There is already a wide spectrum of applications in which ceramics are used under severe conditions; but there are many other areas where needs exist for refractory and corrosion-resistant materials, in which the successful use of ceramics would bring very great benefits. World-wide, there is a high level of interest in new and improved processes for generating, converting and storing energy. These are needed to meet continuously increasing demand, to make better use of the most abundant resources, and to overcome difficulties due to dwindling supplies or escalating costs. There is widespread agreement among scientists and engineers that ceramics have a vital part to play in the successful development and use of energy systems in which environmental conditions are severe.[1] The varying cost and strategic nature of oil supplies have added impetus to research into alternative methods for propelling vehicles; one possibility is by the use of high energy battery systems, such as the sodium/sulphur and lithium/sulphur cells. Such batteries would also be valuable for load-levelling, whereby electricity generated at off-peak times could be stored and used during the periods of greatest demand. The primary objective of research on advanced batteries is to develop cells of high specific energy, that is, high energy storage capacity per unit of weight. The light weight and high reactivity of the lithium/sulphur and sodium/sulphur systems are responsible for their performance advantages over conventional batteries. In addition, the elements are abundant and inexpensive. However, the use of highly reactive elements and compounds creates a need for ceramics capable of withstanding corrosive attack for the life of the cell; these are needed for structural components, such as seals, separators and connectors, and for special functions, for example as solid electrolytes.

The successful use of ceramics in gas turbines would enable higher operating temperatures to be used. Because efficiency increases directly with temperature, and the failure of materials to survive high temperatures is the most important limiting factor, this area has been the subject of extensive research. Ceramics based on silicon carbide and silicon nitride retain exceptional strength and creep resistance to very high temperatures, and are remarkably resistant to oxidising environments. For these reasons they have been widely studied with a view to use as structural components in gas turbines, and for other high-temperature applications. By far the largest volume of research has been directed towards improving and utilising their excellent thermal and mechanical properties. Although the ability to resist chemical attack can be equally important, the effort applied to the characterisation and understanding of corrosion resistance has been relatively small. The successful use of these silicon-based ceramics at high temperatures under oxidising conditions depends on the formation of a protective coating of silica; it is important to consider the possibility that this layer will be removed when contemplating use under potentially reducing conditions, or where the presence of fluxes may arise. Fuel oils commonly contain trace amounts of sodium, sulphur and vanadium; consequently, their combustion products may contain vapours or aerosols of sodium salts or vanadium compounds, which are capable of causing disastrous effects.[2–4] Another aspect of the use of these ceramics in high-temperature engines is the possibility of metal/ceramic interaction. If a structural component is used in hot machinery, it must come into contact with the metal structure at some point; it is therefore necessary to consider the possibility of reaction between them. This is especially likely when the ceramic contains free silicon, which is capable of reacting with most metals to form alloys or silicides.[5]

In a programme to develop ceramic heat exchangers for gas turbines, small amounts of sulphur in the fuel were found to be the cause of disastrous failures when regenerators based on beta-spodumene were given long-term durability tests.[6] This crystalline lithium aluminium silicate was chosen because it has very low thermal expansion, and consequently bodies made from it are very resistant to damage by thermal stress and thermal shock. However, sulphuric acid formed from the sulphur was able to leach out lithium ions, causing changes which eventually led to disintegration of the structure. (This difficulty was later overcome using a process which modified the chemical properties of the ceramic.)

To summarise, a large effort is being applied to the development of technology and engineering systems capable of satisfying the demand for energy. These require materials capable of performing under severe environmental conditions and at high temperatures. Ceramics are expected to be the key to technical and economic success, because they have the potential to offer reliability and durability at a reasonable cost. Furthermore, there are similarities between materials problems in energy systems and those in the manufacture of glass, steel and chemicals and the refining of petroleum; consequently, if the materials science expertise gained from energy research could be applied in these industries, it should be possible to produce more robust plant and equipment, leading to greater reliability and efficiency in production. The prevention of corrosion by the use of the most resistant materials available enables unscheduled shut-down of plant and equipment to be minimised, with consequent savings in materials and labour; it also reduces the possibility of waste and contamination of the products, which would lead to higher costs and deterioration in quality.

There are several reasons why the potential of ceramics as engineering materials is far from being realised, even though they have a range of properties which is unrivalled by other classes of materials. The main reason is the reluctance of engineers to use brittle materials. This is quite understandable, since it is necessary to develop a new design technology; designs must be chosen so that tensile stresses arising from mechanical forces or thermal effects do not reach excessive levels and initiate fracture. A second reason is the common belief, justified to a certain degree, that ceramics are variable in performance, and that ceramic processing needs to be improved in order to achieve greater consistency. In recent years significant technical progress has been made towards the goal of increased reliability, by the use of improved powders, by using techniques such as hot isostatic pressing to reduce flaws, by transformation toughening and by fibre-reinforcement; but for many applications the costs of these improved materials are at present too high.

Another reason is the shortage of reliable and impartial information on the different types and classes of ceramic. Accurate data would enable the user to interpret the claims made for any one material in a true perspective, and make an informed comparative judgement of the best type to use for a given application. It can be very difficult for the non-specialist to assess the corrosion resistance of different ceramics, and in particular, to compare the newer ones such as carbides and nitrides, with the better established materials such as aluminas and porcelains. Firstly, it is common for a term such as 'alumina', 'silicon nitride' or 'silicon carbide', to be used as if it were a single material, whereas each covers a range of products, manufactured by a variety of processes, having different levels of purity, and consequently showing large variations in microstructure and chemical inertness. This frequently leads to inconsistencies and contradictions in the literature; for example, according to Kingery[7] 'Hydrogen fluoride reacts with Al_2O_3, but it is stable in HCl'; whereas according to Ryshkewitch[8] 'Concentrated hot hydrochloric acid also attacks alumina . . . cold hydrofluoric acid has almost no effect'. When assessing statements like this, it is always important to consider whether the results were based on experiments with fine powder, a pure single crystal, a pure sintered body, or a component containing additives; the results can be very different. It is also desirable to know the temperature, concentration of reagent and period of exposure. Often these experimental details are not given, and consequently the value of the observation is dubious. When considering ceramics for a particular application, the user often finds that suppliers give optimistic descriptions of conditions under which performance is deemed satisfactory, but there is an absence of information about environments which cause deterioration and failure. Finally, the information that does exist is scattered in a great variety of brochures, journals, books, government reports and conference proceedings, and is not available in a form which would enable one type of ceramic to be compared with another.

1.2 Purpose of the book

The primary purpose of this book is to provide a collection of information from these varied sources, and so give an impartial guide to the selection and proper use of different types of ceramic in corrosive environments. Engineers are much more familiar with metals and metallic alloys than with ceramics, and naturally prefer to use them whenever possible, since they have the great advantages of malleability, ductility and toughness, and are readily shaped by machining. However, situations frequently arise where metallic materials fail to meet one or more of the service requirements, and it is necessary to consider replacing a metal component with a ceramic part, or to use ceramic materials, or a particular type of ceramic, for the first time. In these circumstances, the user may have difficulty in choosing a suitable material, either because he is unfamiliar with the nature of ceramics, or because of a shortage of reliable information about their properties. The book is therefore mainly intended for design and development engineers who are concerned with plant, equipment, devices and components which are exposed to corrosive media. These applications cover a wide spectrum of products, including those used in the chemical, metallurgical and glass-making industries, and also in such diverse fields as electrical engineering, electric power generation and storage, gas turbines, catalyst supports and heat exchangers. The book should also be of value to workers in research and development who are faced with problems in material selection, and to ceramic technologists and materials scientists, particularly those concerned with the development of new and improved products, who need an understanding of the causes of deterioration and failure.

1.3 What is a ceramic?

The word 'ceramic' was originally applied to objects made from clay, shaped at ambient temperatures, and permanently hardened by heat. For centuries a ceramic could be defined by these characteristics. However, in the present century, the demand for more sophisticated materials with improved properties has led to the development of higher-grade products, which are also described as ceramics, but which do not conform to the original description; in fact, no satisfactory definition now exists. According to Kirk-Othmer[9] 'Ceramics comprise all engineering materials or products that are chemically inorganic, except metals and alloys, and are usually rendered serviceable through high-temperature processing'. Obviously, this description could include a large group of materials, including coarse refractories, pottery, domestic porcelain, and building products such as bricks and tiles; none of these classes will be described in detail. The term 'ceramic' will be used in this book to cover materials derived from the compounds listed on page xi. They all conform to the description given, but since glasses and single crystals will only be mentioned in passing, they have the additional characteristic of a polycrystalline structure. They are always brittle, and commonly hard, suitable for use at high temperatures, and resistant to corrosive substances. The main emphasis will be on ceramics which can be produced with high strength in accurate shapes, and can therefore be used in engineering where the ability to sustain mechanical stress is required; these are often referred to as 'engineering ceramics'. Of these, the oxides form the most widely used group, whereas the non-oxides such as carbides, nitrides and borides have been developed for special applications in which other materials fail. A specific aim is to enable a user to compare the more recently developed ceramics with the well-established ones, and so provide an aid to material selection.

Coarse-textured refractories have great industrial importance, and are used on a massive scale for such applications as blast furnace and glass tank construction; however, they are beyond the scope of this book, and will only be mentioned briefly. In general, they are developed for specific purposes, and consequently there is less need to compare one type with another. Nonetheless, the discussions of mechanisms of attack, and principles governing corrosion resistance will be relevant to an understanding of their performance. In addition to the technical and engineering ceramics, a few non-ceramic materials such as vitreous silica have been included since a user may wish to compare their properties with those of ceramics.

1.4 What is corrosion?

The word 'corrosion' is used to describe the eating away of a solid material by its environment; it is most commonly applied to the deterioration of metals due to chemical attack which is oxidising in nature. The term can equally well be used for other classes of material, and when applied to ceramics is not restricted to oxidising reactions, but encompasses those in neutral and reducing conditions as well. It is common for the mechanism of reaction to involve preferential intergranular attack, and this can produce changes in properties, without necessarily causing any alteration in dimensions or appearance. The word 'corrosion' will therefore be used to describe all degradative changes induced by chemical attack, whether they affect appearance, properties or structure, resulting from exposure to hostile species such as acids, alkalis, halogens, hot gases, fused salts and molten metals.

CHAPTER 2

Manufacture of ceramics

2.1 Introduction

In this chapter a brief account of common fabrication processes is given. The process used determines the chemical composition, microstructure, porosity and surface texture of the ceramic, and these in turn regulate resistance of the product to chemical attack. The traditional methods used for clay-based ceramics involve three basic operations: firstly the raw materials are prepared and mixed together, secondly this mixture is formed into the required shape, and thirdly the component is fired so that a permanent solid results. These methods will not be described in detail, as they are fully discussed elsewhere; a very lucid introductory account has been given by Chandler,[10] and a much more comprehensive treatment by Kingery and others.[11] It has been necessary to modify these methods when dealing with non-clay compositions, and to develop entirely new techniques for some of the more advanced materials. The descriptions will not be detailed, but are intended to highlight those aspects of the fabrication process which have a determining influence on corrosion resistance. The most important of these is the chemical nature of minor constituents.

Apart from this dependence of corrosion resistance on the fabrication method, there is another important reason why it may be helpful for engineers to know something about the manufacture of ceramic articles. When using metallic materials, it is customary to shape the components required by machining blanks bought from a manufacturer. With a few exceptions, it is not economically feasible to produce ceramic articles in this way. Because of the hardness, wear resistance, and lack of toughness of ceramics, such machining usually needs to be done with diamond tools, and is slow and expensive. Consequently, it is usual for the shaping to be carried out by the manufacturer, who chooses a fabrication method which is appropriate for the particular shape required. Because of this, the design engineer must not only find a ceramic which is capable of giving the properties required, but he must also ensure, by collaboration with the manufacturer, that the component is amenable to fabrication procedures which yield these material characteristics in the final product.

2.2 Fine-grained clay-based ceramics

2.2.1 Introduction

The clay-based aluminosilicate ceramics form a group which is used on a large scale, and for a wide variety of uses in the chemical, metallurgical and related industries. The bodies are produced from mixtures of clays, feldspars, and more inert non-plastic ingredients such as flint or quartz. The mixture is shaped by a suitable method, usually dried, and then fired. Firing causes partial fusion, reduces porosity, and yields a hard product consisting of crystals bonded together by glass. Of the common ingredients, flint forms the skeleton of the structure, clay acts as a filler, and feldspar acts as a flux. The flint skeleton limits shrinkage and distortion on drying and firing; the clay renders the body plastic during shaping and gives it strength when dried; the feldspar fuses on heating and acts as a glass-forming agent by dissolving part of the flint and clay. Naturally, it is necessary to vary the ingredients, shaping process and firing schedule according to the shape required, and the purpose for which it is intended.

2.2.2 Stoneware

Stoneware is made from a mixture containing a large proportion of highly plastic clays, and is shaped by conventional techniques such as slip-casting and extrusion. It is commonly fired to 1150–1250 °C, the schedule being chosen to eliminate open porosity, or reduce it to a very low level, while avoiding overfiring which would cause undesirable deformation.

Stoneware is used for domestic applications such as drainpipes and sewer pipes, and suitably formulated chemical stoneware is widely used in the chemical industry, especially for handling mineral acids and other corrosive liquids. It can be formed into articles of almost any shape, and in large sizes, and is used for such components as tanks, pipes, jars, towers and tower packings.

2.2.3 Porcelains

The fabrication techniques and applications of chemical porcelain are similar to those of chemical stoneware; it is stronger mechanically and has superior resistance to chemical attack, but cannot be made into such large pieces. It contains a larger proportion of alumina, and is suitable for use at higher temperatures, and for applications involving some degree of thermal shock. Like chemical stoneware it has good resistance to acids (with the exception of hydrofluoric) but it is said to be significantly better in resisting alkali solutions, although both materials are attacked to some extent.

In addition to chemical porcelain, a range of similar materials is available, suitable for use at much higher temperatures. These high-temperature porcelains have good resistance to thermal shock, and are used for sheaths, tubes and insulators in pyrometry, and for furnace and kiln construction. The most refractory products in this class are impervious mullites, which are usable to about 1650 °C.

2.3 Glass-ceramics

In 1957 a new type of ceramic was discovered by Stookey at Corning Glass Works in the United States, when a piece of a photosensitive glass was