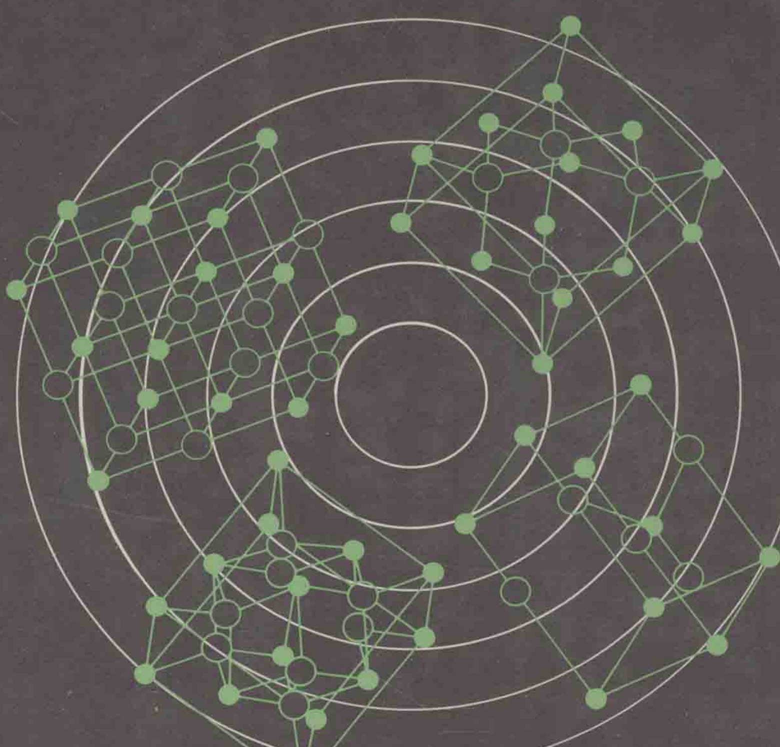
INTRODUCTION TO FINE CERAMICS

APPLICATIONS IN ENGINEERING

edited by

NOBORU ICHINOSE



Introduction to Fine Ceramics

Applications in Engineering

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Preface

Recently, 'new ceramics' or 'fine ceramics' has become a topic of discussion. Fine ceramics, especially, has been in the newspapers and weeklies, since the Ministry of International Trade and Industry decided in 1981 to promote and develop it as a part of its 'Next Generation Industries Technology Development Program,' with investments of around ¥ 14 billion (US$ 58.3 million) over ten years. In addition, makers and users of fine ceramics formed the Fine Ceramics Society in July 1981. The goals of this society are promotion of research and information exchange in manufacture and utilization, market research, technology development, positive international exchange, and improvements in the fundamentals of the fine ceramics industry. Thus the term 'fine ceramics' has become better-known, and has promoted a discussion about its exact meaning. Currently there is no exact definition and, according to the user, 'fine' could mean anything from little, delicate or beautiful to high level.

Tentatively, then, I will give a narrow definition. Ceramics have many properties, but one can think of ceramics that have special practical properties, as well as those with specific unusual properties, as fine ceramics. One can say that fine ceramics is functional ceramics.

Accordingly, one can see that, even though there have been many books specializing in fine ceramics lately, they are quite difficult. There have been almost no illustrative, easy-to-understand books on the subject. This book uses a question and answer format to provide just that kind of explanation of fine ceramics. The book is organized as follows: Chapter 1, Fundamentals of Ceramics: Questions and Answers; Chapter 2, Structural Ceramics: Questions and Answers; Chapter 3, Electronic Ceramics: Questions and Answers; Chapter 4, Glass and Optical Fibers: Questions and Answers; and finally, Chapter 5, New Technology of Ceramics: Questions and Answers. In this way the book tries to give the reader a concrete picture, including tables and diagrams, of fine ceramics from the basics to the most recent research.

In the future it seems that fine ceramics will continue to develop. And if this book helps engineers and materials researchers to a deeper understanding or helps pave the way for new engineering or materials development even a little, the writers will be gratified.

Finally, we wish to express our appreciation and thanks to the publishers, Ohmsha, Ltd and John Wiley & Sons Ltd. Their cooperation and hard work have been essential to its completion. Also, a personal note, I was kindly allowed to dedicate the book to my beloved daughter who died at the age of thirteen while I was compiling the original manuscript.

Noboru Ichinose

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Contents

1 Fundamentals of Ceramics: Questions and Answers

Chapter 1 will touch upon the fundamentals of ceramics. The differences between ceramics, metals and organic materials, microstructures, and grain boundaries will be mentioned. Powder synthesis, forming processes, and sintering processes will be explained. Sintering processes such as hot pressing and HIP will be commented on. Why ceramics are translucent, why thay are strong at high temperatures, and some more recent topics will be touched upon.

1.1 WHAT ARE CERAMICS AND HOW DO THEY DIFFER FROM METALS AND ORGANIC MATERIAL?

In our society, industrial products are classified in three categories: metals like iron, copper, and aluminum; organic materials like epoxy resins and rubber; and ceramics like porcelain, refractories, and electronics wares (Fig. 1.1).

The term 'ceramics' comes from *keramos*, the ancient Greek word for objects made of fired clay. While retaining this original meaning, the word has also come to designate one of the three main material categories. It has taken on much of what was once included in 'brickmaking', 'pottery', and 'glassmaking'.

What are the main features of the three kinds of materials, and what are the differences between ceramics and the others? Basically, they are a product of the differences in chemical bonding. The consequences are remarkably different physical and chemical properties, as well as different manufacturing processes. Let us compare these materials in more detail.

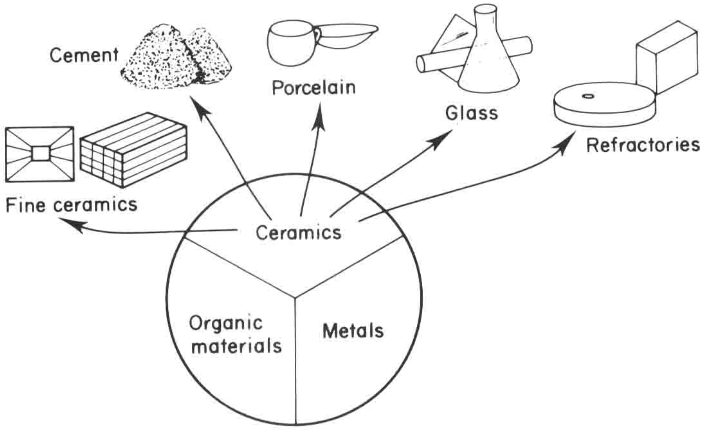

Fig. 1.1 Ceramics: one of the three main product categories

(1) Metals

Chemical bonding in metals, or metallic bonding, is a binding of atoms to other atoms by free electrons. There is good heat and electrical conductivity, non-penetration and reflection of light, and toughness, all of which can be explained by the existence of these mobile electrons.

(2) Organic Materials

Organic materials are compounds of carbon, hydrogen, and oxygen which are found in living organisms, regardless of molecule size. A chain of carbon atoms is formed, to which hydrogen and oxygen are added. The chemical bonding between these non-metallic elements, through which groups of molecules are formed, is usually called covalent bonding. The force, van der Waals force, holding the molecules together is weak. Consequently, the melting points are low, and these materials are characteristically easily shaped and processed.

(3) Ceramics

Almost all ceramics are compounds of the electropositive and electronegative elements of the periodic table. Mostly the bonding is ionic, but in a few cases, covalent or metallic bonding occurs. There are also numerous configurations for each combination of elements, and therefore, various material functions. The common features of these materials are:

(a) high heat resistance
(b) electrically insulating or semiconducting with various magnetic and dielectric properties

(c) strong resistance to deformation, brittle fracture
(d) low toughness.

These properties are sometimes advantageous and sometimes not. Yet technical developments have tended to make use of the good properties and overcome the bad ones. New ceramics have been developed, studied, and kept in the scientific limelight. These are what have been called 'new ceramics' or 'fine ceramics'.

In Table 1.1, ceramics are classified according to application. Although, in the strictest sense, glass should be separated from ceramics, it is included here in concurrence with the above definition. A further division could also be made, between the ceramics that have been used for centuries (traditional ceramics) and the new attention-getting functional materials and machine materials (fine ceramics).

Table 1.1 Ceramics groups (following the *Ceramic Engineering Handbook*)

1. Glass, Enamel		1. Cosmetics
2. Porcelain		2. Fluorescent, phosphorescent materials
3. Refractories, Insulation		3. Man-made minerals
4. Grinders, Sharpeners	→	4. Cermets, ceramic tools
5. Cement, Plaster, Lime		5. Nuclear reactor materials
6. Carbon products		6. Catalytic carriers
7. Electronic ceramics		7. Casting sand
8. Others		8. Non-metallic heat-generator

1.2 WHAT IS FINE CERAMICS?

Usually, ceramics are oxides or non-oxides composed of metallic and non-metallic elements (excluding carbon). Therefore, there are many kinds of ceramics with functions in many fields. In Fig. 1.2 and Table 1.2, the concepts of fine ceramics and the function–material–applied product relationships of oxides and non-oxides are shown. A study of these charts should provide an adequate summary of the many functions of ceramics.

Recently it has been said that 'fine ceramics' is used to designate the ceramics which have high additive value. What, then, is fine ceramics? The specialized functions exhibited by the materials in Table 1.2 cannot be obtained by simply pressing and sintering unrefined raw material. It is necessary to synthesize ceramics using highly refined raw material, rigorously controlled composition, and strictly regulated forming and sintering. The ceramics obtained by this type of process are called 'fine ceramics'. However, this term is not yet completely fixed in meaning. In a broad sense, all of the materials in Table 1.2 are fine ceramics, but in a narrow sense, fine ceramics is limited to the ceramics used as machine materials. Even now disputes as to what to include continue.

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Table 1.2 Functions and practical applications of ceramics

Functional group	Oxide ceramics			Non-oxide ceramics		
	Function	Materials	Application	Function	Materials	Application
	Insulating	Al_2O_3, BeO	Substrates	Insulation	C, SiC	Substrates
	Dielectrical	$BaTiO_3$	Capacitor	Electrical conductivity	SiC, $MoSi_2$	Heat generator
	Piezo-electronics	$Pb(Zr_2, Ti_{1-2})O_3$, ZnO, SiO_2	Oscillator, ignition junction, Surface elastic wave delaying junction	Semi-conductivity	SiC	Varistor, lightning shunt
Electric, electronic functions	Magnetism	$Zn_{1-2}Mn_2$	Memory, operation junction	Electron emission	LaB_6	Electron gun thermal anodes
		Fe_3O_4	Magnetic core			
	Semi-conductivity	SnO_2,	Gas-sensor			
		$ZnO–Bi_2O_3$ $BaTiO_3$	Varistor Resistance junction			
	Ionic conductivity	β-Al_2O_3,	NaS battery			
		Stable ZrO_2	Oxide-sensor			

Table 1.2 (*contd.*)

Functional group	Oxide ceramics			Non-oxide ceramics		
	Function	Materials	Application	Function	Materials	Application
Mechanical functions	Wear resistance	Al_2O_3, ZrO_2	Polishing materials Grindstones	Wear resistance	B_4C, diamond	Wear-resistant materials, grindstones
	Machineability		Cutting tools	Machineability	C–BN, TiC, WC, TiN	Cutting tools
				Strength functions	Si_3N_4, SiC Sialon	Engines, heat resistors Anticorrosives, tools
				Lubricating functions	C, MoS_2, h-BN	Solid lubricants, mold-releasing agents
Optical functions	Fluorescence	Y_2O_2S: Eu	Fluorescent materials	Transparency	AlON, nitrogen glass	Windows
	Transparency	Al_2O_3	Sodium lamp Mantle tube	Reflectiveness	TiN	Light collectors
	Optical polarization	PLZT	Optical polarization junction			
	Light conductivity	SiO_2, multiple-constituent type glass	Optical communication fibers			

Table 1.2 *(contd.)*

Functional group	Oxide ceramics			Non-oxide ceramics		
	Function	Materials	Application	Function	Materials	Application
	Heat resistance	Al_2O_3	Structural refractories	Heat resistance	SiC, Si_3N_4, h-BN, C	Various refractories
Thermal functions	Heat insulation	$K_2O{\cdot}nTiO_2$, $CaO{\cdot}nSiO_2$, ZrO_2	Heat-insulating materials	Heat insulation	C, SiC	Various heat insulators
	Heat conductivity	BeO	Substrates	Heat conductivity	C, SiC	Substrates
Nuclear power related functions	Nuclear reactor materials	UO_2 BeO	Nuclear fuel Moderator	Nuclear reactor materials	UC C, SiC C B_4C	Nuclear fuel Coated nuclear fuel Moderator Control rod material
Biochemical functions	Teeth & bone materials	Al_2O_3, $Ca_5(F, Cl)P_3O_{12}$	Artificial teeth & bones	Corrosion resistance	h-BN, TiB_2 Si_3N_4, Sialon	Evaporation chamber Pump materials, others
	Carrier ability	SiO_2, Al_2O_3	Catalytic carriers		C, SiC	Anticorrosives

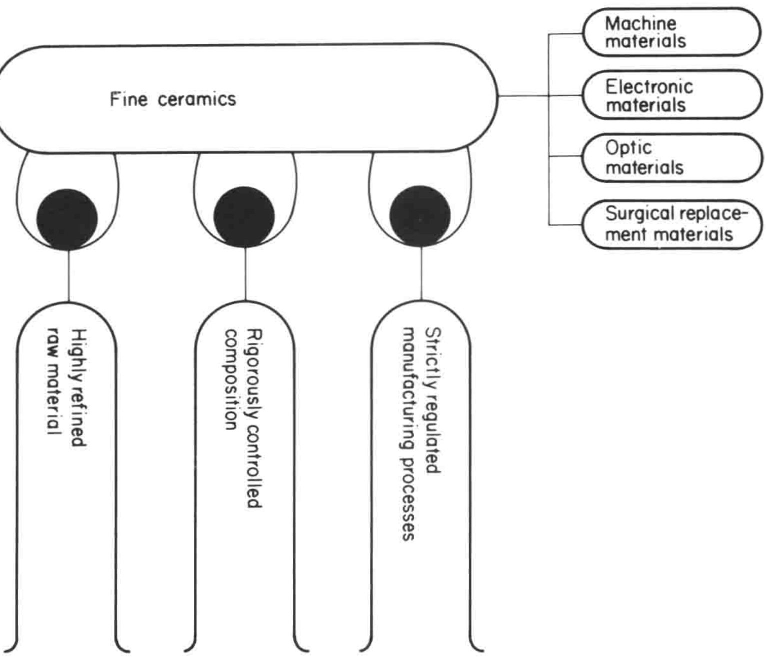

Fig. 1.2 General concepts of fine ceramics

The above definition is limited to sintered ceramics, but in Table 1.2, single crystals, thin film, and glass are also included. It is somewhat contradictory to include these, but they are included because of their functional applications. Also, besides, 'fine ceramics', many other terms have been coined to describe these materials: 'new ceramics,' 'special ceramics,' 'modern ceramics,' 'engineering ceramics,' 'electroceramics,' etc., have all been used. Lack of standardization has caused much complexity, but fine ceramics technology is that which gives ceramics additive value. And in their manufacture it is important to control the powder and the microstructure. The rest of this book deals with a number of techniques necessary for the production of high-quality fine ceramics.

1.3 WHAT IS THE CRYSTAL STRUCTURE OF CERAMICS

Ceramics have inorganic structures. Sometimes there are glass-like amorphous structures, but almost all ceramics have a crystal structure. Here, then, is an outline of structures.

Matter can exist in three different states: solid, liquid, or gas (Fig. 1.3). These states are distinguished by interatomic distances. The atoms or molecules in a gas are diffused in space. As they become liquid and then solid, the regularity of their arrangement is increased. In the solid state, the attractive force overcomes the thermal effect which separates the atoms, and they begin to occupy fixed sites.

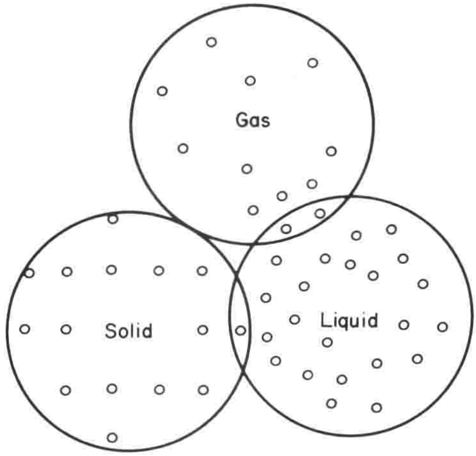

Fig. 1.3 Molecular positions in the three states of matter

In order to understand crystal structure, it is necessary to know something about atomic structure, but explaining atomic structure in detail is not within the scope of this section, so it will only be touched upon in relation to bonding strength in ceramics. There are ionic bonds, covalent bonds, van der Waals bonds, and metallic bonds. Oxide ceramics mainly have ionic bonding. Covalent bonding, which is strongly directional, can be seen in non-oxides, silicon, etc. The crystal structure of oxides is governed by the close-packing of O^{2-} ions, with cations situated among them. In this way polyhedra are formed with cations surrounded by O^{2-} ions. The number of anions surrounding a cation is called the 'coordination number.' This number is determined geometrically by the ratio of the ionic radii. As a result, calculated predictions closely agree with the real polyhedra. Triangular, tetrahedral, rhombohedral, octahedral, cubic, and close-packed configurations of anions exist. The real structure is formed spreading out in three dimensions.

Some minerals which are identical in composition have different crystal structures and different chemical and physical properties. Such minerals are said to be 'dimorphic.' The assumption of two or more crystal structures by the same substance is called 'polymorphism.' For example, there are: quartz, cristobalite, and tridymite configurations of SiO_2; rutile, anatase, etc., configurations of TiO_2; and diamond and graphite configurations of carbon (C). The polymorphic crystal structures are called 'modifications' of a substance, and the change from one crystal structure to another is known as 'transformation.' It is helpful to learn these terms because they crop up all the time.

Several typical examples of oxide structure groups are: rock salt (NaCl), cubic; zincblende (β-ZnS), cubic; wurtzite (α-ZnS), hexagonal; fluorite (CaFe), cubic; rutile (TiO_2), tetragonal; corundum (α-Al_2O_3), hexagonal; perovskite ($CaTiO_3$); spinels like magnesium aluminate spinel ($MgAl_2O_4$)

(see Fig. 1.4). Each structural group has similar chemical and physical properties, and these groups are the materials known as ceramics.

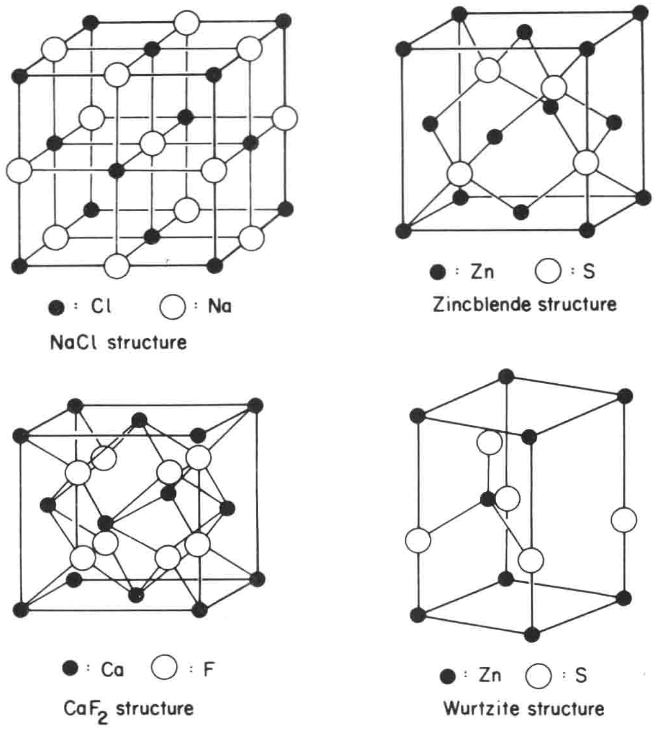

Fig. 1.4 Representative crystal structures

1.4 WHAT IS THE MICROSTRUCTURE OF CERAMICS

The microstructure of polycrystalline ceramics is usually complex, as is shown by Fig. 1.5, and distinguished by the existence of grain boundaries, which are not seen in single crystals. Also, the existence of pores, imperfections, and multiphase compositions makes for great variety. Up to now, grain boundaries and additional phases were thought to be undesirable, and the goal was to eliminate them and obtain a structure as close to single crystals as possible. However, new processes have been found that make positive use of these surfaces and grain boundaries, and functional ceramics in which these properties are important are developing rapidly.

Fig. 1.5 can be used to explain what is meant in terms of grain boundaries. In the grain boundary region, energy is increased, so impurities tend to gather there. The impurities exist as a second or third phase among the constituent particles or segregate into the grain boundaries. With an increase in the amount of impurities and additives, the microstructure shifts from (a) to (c).

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