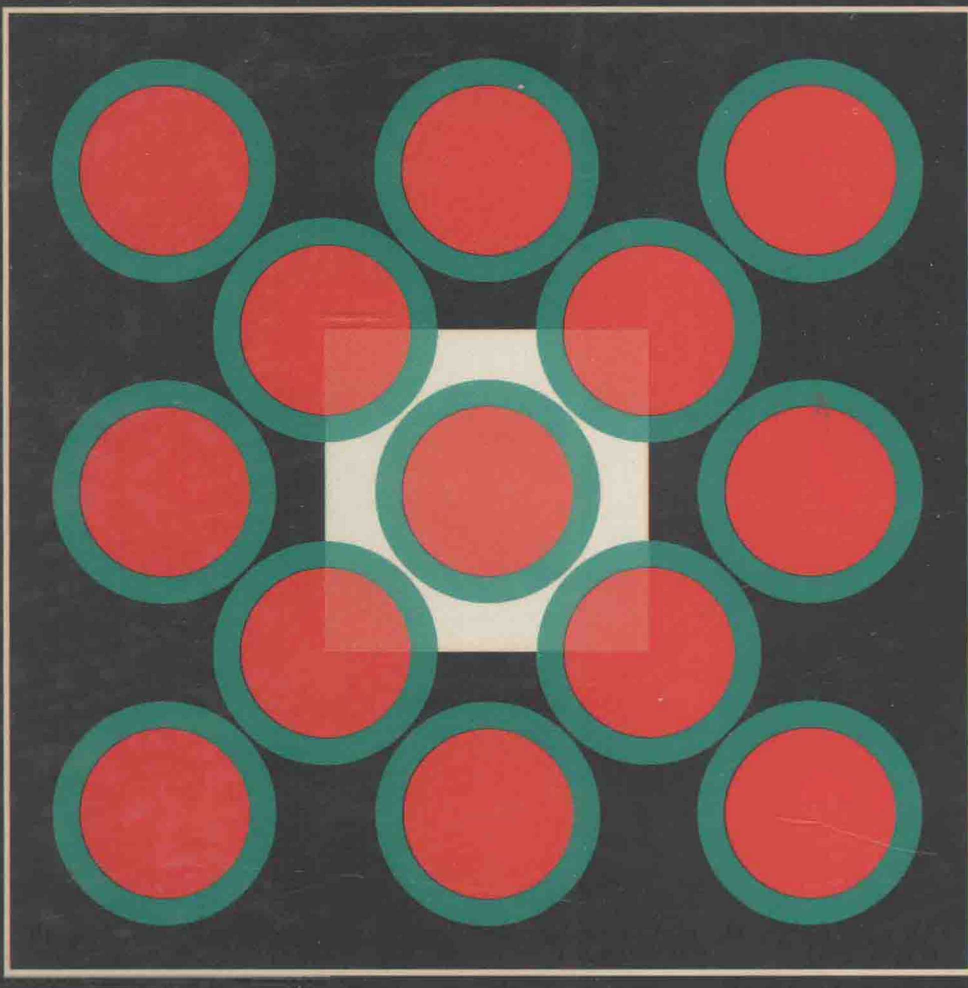
FINE CERAMICS

Edited by

Shinroku Saito



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PREFACE

There were two so-called new material booms after World War II, in the mid-1950s and mid-1960s. We are now in a third boom which began slowly but is now gaining momentum. The significant difference in this boom is the development of tertiary industrial infrastructure.

Functional ceramics for electronics, opto-electronics, and related devices have been developed with considerable success. However, structural ceramics development has been slower despite the demand by the military and other sources for high temperature material capable of withstanding high mechanical stress, such as in ceramic turbines.

This book on ceramics development consists of four chapters. The first chapter concerns ceramic fabrication, including recent developments in powder synthesis through hot press and hot isostatic press. The second chapter discusses the relationship between properties and structures, involving observation methods. The third chapter covers structural ceramics made from oxides and nonoxides, through composites and their evaluation. The last chapter describes various recently developed ceramics for electronics.

The authors would be very pleased if this book were accepted abroad as a greeting from Japan to colleagues in the ceramics industry worldwide, a step toward future communication and deeper understanding.

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INTRODUCTION

Shinroku Saito

Japanese skills in porcelain have been well known internationally since before World War II. After the war, Japanese technology in fire brick supported the development of its famous steel industry. However, these achievements belong to the field of "old" ceramics, now made obsolete by research and development in the field of advanced ceramics.

The terms "fine ceramics" and "new ceramics" are often used interchangeably in Japan to denote the products of this R&D work. The former term is an official technological designation established by Japan's Ministry of International Trade and Industry (MITI) to characterize ceramics of a texture much finer than that of traditional types of ceramics such as bricks, sanitary ware, and household porcelain. (Additionally, there are many names for ceramics recently developed by high technologies, including advanced ceramics, high-tech ceramics, high-performance ceramics, engineering ceramics, super-ceramics, ultra-ceramics, and hyper-ceramics.) Some functions and applications of fine ceramics, including thermal, mechanical, biological, magnetic, optical, and nuclear applications, are shown in Figure 1.

Fine ceramics can be roughly classified in two categories: functional and structural. The former term is used for ceramics that perform electronic, electromechanical, optical, opto-electronic, or magnetic functions. Defining the latter category is more complicated, as

Functions and applications of fine ceramics (examples)

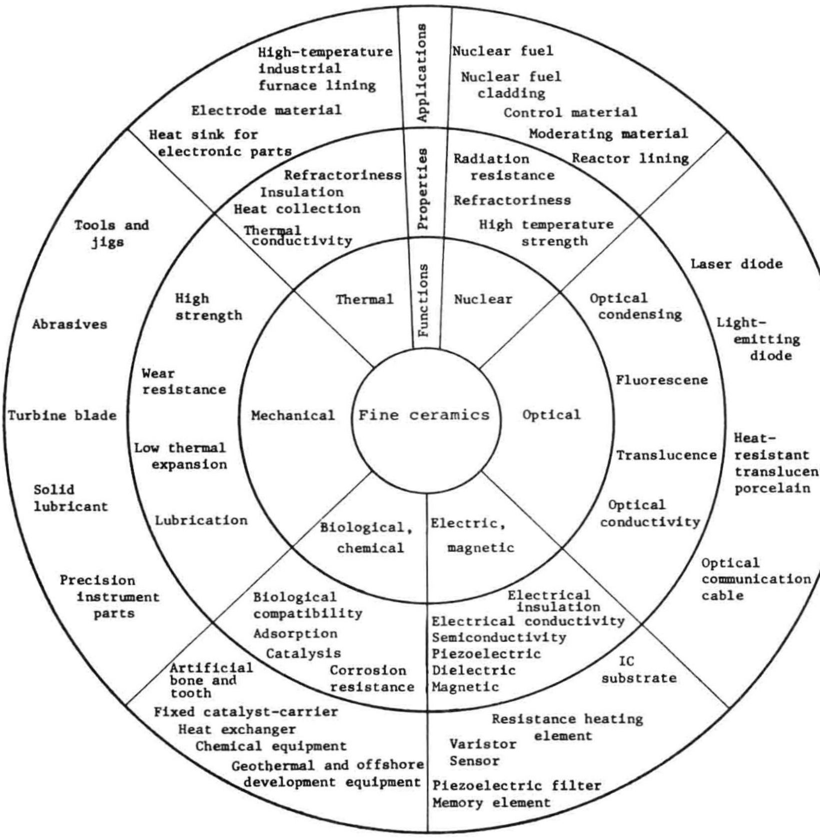


Figure 1 Some functions and applications of fine ceramics (from Japan Fine Ceramics Assoc., "Survey of Trends in Development of Fine Ceramics Technologies and Situation of Development of Related Equipment," April 1983).

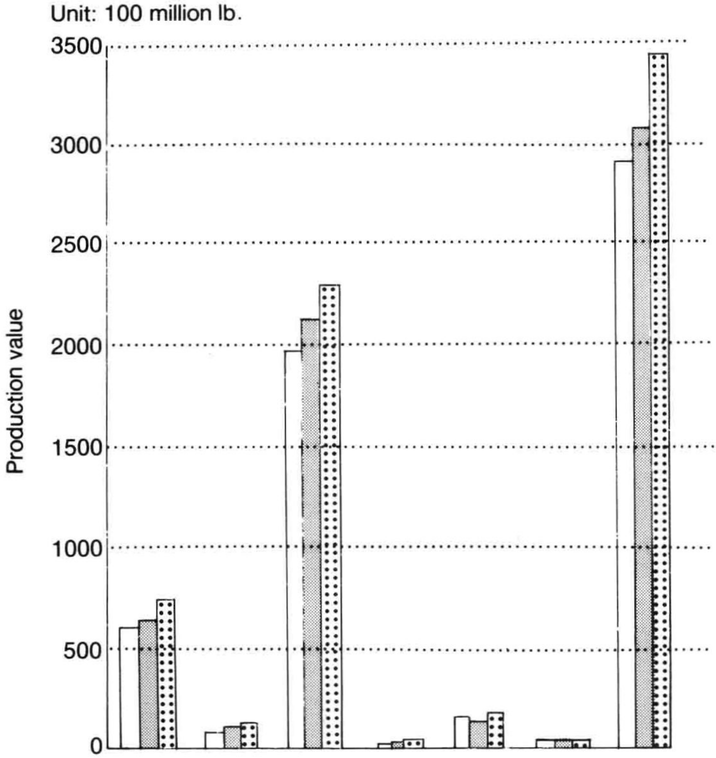
the term "structural ceramics" does not denote the customary use of ceramic products for structural materials such as bricks, roofing tiles, and cement. Thus, "fine" must be emphasized to underscore the revolutionary applications of new ceramics for structural materials in machinery, especially for high-temperature machinery parts. Although ceramics have been well known as excellent refractory materials for products such as fire brick, they could not be successfully utilized under high thermal and mechanical loading until fine ceramics were developed using pure, ultra-minute particles whose green compacts are sintered, machined, and finished under highly controlled conditions and strict quality control.

The production values of fine ceramic materials for various purposes are given in Figure 2. More than 60% of fine ceramics are used for electromagnetic parts; 25–26% are used for machine parts and 6–7% for biochemical purposes. These percentages have not fluctuated much over the years. Although thermal uses and optical parts constituted only 4% and 0.7%, respectively, of fine ceramic usage in 1981, both increased to 4.5% and 1.5% in 1983. If we use 1981 production as the base (i.e., 1981 = 100), we see that the increase in thermal uses up to 1983 is 118, and that of optical parts is 250.

Analysis of these data reveals that the market for structural fine ceramics is still immature. Although large investments have been made in structural ceramics for the purpose of creating a sizable market, the main products are still cutting tools, abrasives, grinding balls and mills, mechanical seals, small chemical pumps, and the like. However, investment in the electromagnetic ceramics field is increasing because of a widening market, severe competition, and the emergence of unexpected new materials and inventions. Such investment accounts for more than 10% of all national research expenditures, although business sales are still only about 1% of total earnings.

Recently, the popularity of fine ceramics in Japan has grown so much that one could say that a "ceramics fever" has broken out among Japanese ceramics manufacturers and other industries, although foreign manufacturers view this trend suspiciously. Will fine ceramics be the star industry of the 1990s? Will fine ceramics be at the forefront of a new "Materials Revolution"? Only the future will tell.

The Materials Revolution can be traced back to the Industrial Revolution, which began with many mechanical inventions such as the power loom and the steam engine. Steelmaking during the Industrial Revolution first encountered problems in using charcoal for fuel. Charcoal steel required tremendous amounts of wood and afforded only a limited scale of manufacture. The need for wood raised ecological problems, while the problems of scale affected the quality of the steel. If the coke furnace had not been invented, one could easily surmise that the Industrial Revolution would have been halted or significantly slowed by limits in available wood resources. But new technologies in steelmaking facilitated large-scale production, resulting in fairly good quality control. Thus, the invention of new steel-manufacturing methods helped to promote the Industrial Rev-



	Year	Mechanical	Heat-resistant	Electro-magnetic	Optical	Chemico/biological	Others	Total
	1981	614	94.9	1,970	17.2	162	43.9	2,902
	1982	624	112	2,119	29.4	156	45.7	3,086
	1983	740	135	2,304	42.3	186	51.2	3,458

Mechanical members: Cutting tools, mechanical seals, pumps, pump parts, crushing/pulverization members, valves
Heat resistant members: Adiabatic/heat insulation members, heat transmission/radiation members, heating elements, high-temperature corrosion-resistant members, crucibles
Electromagnetic materials: Magnetic members, capacitors, IC circuit substrate, IC baseplate packages, electrical insulation members, varistors, gas sensors
Optical materials: Light permissive members, optical fibers
Chemico/biological materials: Catalyst carriers, catalysts, prosthetic teeth and bones
Others: Artificial gems, filtration materials

Figure 2 Production values of fine ceramic materials.

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olution; and, in short, a Materials Revolution occurred simultaneously with the Industrial Revolution.

Arguably the most important aspect of the Industrial Revolution is the drastic change in human thinking that it engendered, especially with regard to materials. In the past, every kind of material, even if artificial, was regarded as a result of natural forces; the human element was given only marginal credit. Confidence in human capabilities has risen greatly since then, resulting in the emergence of the material design concept. This conceptual change has given birth to a number of new processes.

Functional ceramics are fascinating materials from the perspective of both design and processing. Much of the basic research in ceramics is concentrated in this area. Several years ago, Japan's National Research Institute of Inorganic Materials (NRIIM) reported success in achieving single-crystal growth of LaB_6 and announced the commercial applicability of the new material as a strong new optical beam source for LSI processing. NRIIM is now carrying out research on rare-metal doped perovskite such as $Ba^{2+}_{0.9}La^{3+}_{x}Ti^{4+}O_3$ for use as semiconductors.

PZT, PLZT, and $(Pb_{1-x}Na_yO_{x-y})(Zr{\cdot}Ti)O_3$-type dielectric ceramics and the like are also attracting wide interest from researchers. Although ZnO has already achieved a high commercial reputation as a result of the work of Matsushita Electric Company, there is still a strong research interest in developing various other applications, including varistors, surface elastic-wave filters, electronic photograph sensitizers, synthesizing menthanol catalyzers, and gas sensors. ZnO and TiO_2 have in the past been used only for pigments and fillers; however, they and their derivatives have now become very important electronic materials. Recent research on TiO_2 shows a promising potential for its application as a catalyzer for separating oxygen and hydrogen from water using energy from the sun, thereby opening up new possibilities for various semiconductors such as CdS and $SrTiO_3$.

Moreover, new technologies such as rapid quenching of molten states and shock-wave treatment on powder and microbeam techniques are opening the way for beneficial uses for functional ceramics. Rapidly quenched $LiNbO_3$ and $PbTiO_3$, for instance, have shown very high dielectric constants. Solid electrolytes can be used in gas sensors, ion sensors, electronic memory elements, batteries, and ion pumps. These are usually made of polycrystalline ceramics. Beta-aluminum is presently the most promising candidate for use in sodium-sulfur batteries. Partially stabilized zirconia is now used as an excellent oxygen sensor in steelmaking and as an oxygen pump to adjust biological oxygen environments. Development of amorphous-state electrolytes by rapid quenching is expected to provide various other future applications. (The oxide magnet was invented by Professors Y. Kato and T. Takei long before World War II.)

Much research has been carried out on $Zn_{1-x}Mn_xFe_2O_4$ (soft), α-Fe_2O_3 (soft), and $SrO \cdot 6Fe_2O_3$ (hard). Transparent and translucent ceramics are also very important products. Transparent alumina tubes are already being used for sodium lamps. However, the transparent sialon produced by NRIIM is presently regarded as the most attractive material for high-temperature windows through which elevated temperature states of materials and processes can be directly observed. Additionally, many kinds of thermistors, varistors, gas sensors, electric resistance heaters, and nonlinear semiconductors such as the CdS-Cu_2S junction have already been or are being developed in Japan. Because of their applicability as semiconductors, electronic elements, integrated circuits (ICs), large-scale integrated (LSI) circuits, and ceramic substrates and packages, transparent and translucent ceramics promise to foster lucrative and prosperous industries. Production trends for products made from electronic, magnetic, and optical ceramics from 1981 through 1983 are shown in Figure 3.

The costs of R&D for structural fine ceramics cannot yet be recovered. However, R&D has been greatly stimulated by government support through the Project for Future Fundamental Industrial Technology. This project was started by MITI three years ago to promote basic industrial technologies ranging from fine ceramics to biotechnology. The reason such a project was implemented lies in the fact that various government projects such as the Sunshine Project, the Moonlight Project, and the Large-Scale Project have been hampered by the lack of practical basic technologies, including a lack of knowledge about new materials. The project was also intended to counter criticisms from abroad that Japan has always received a "free ride" on foreign technology. In this context, MITI chose to implement a project with a definite selection standard; its support would be limited to fields too risky for private companies to carry out R&D, and to immature markets. Consequently, only structural ceramics was adopted under the project, and the development of functional ceramics was left to market forces.

A research association was recently established to carry out a cooperative study among the 15 member companies constituting the leading users and manufacturers of fine ceramics. The study emphasized the development of silicon carbide and silicon nitride as well as the following three subjects: refractory ceramics for elevated-

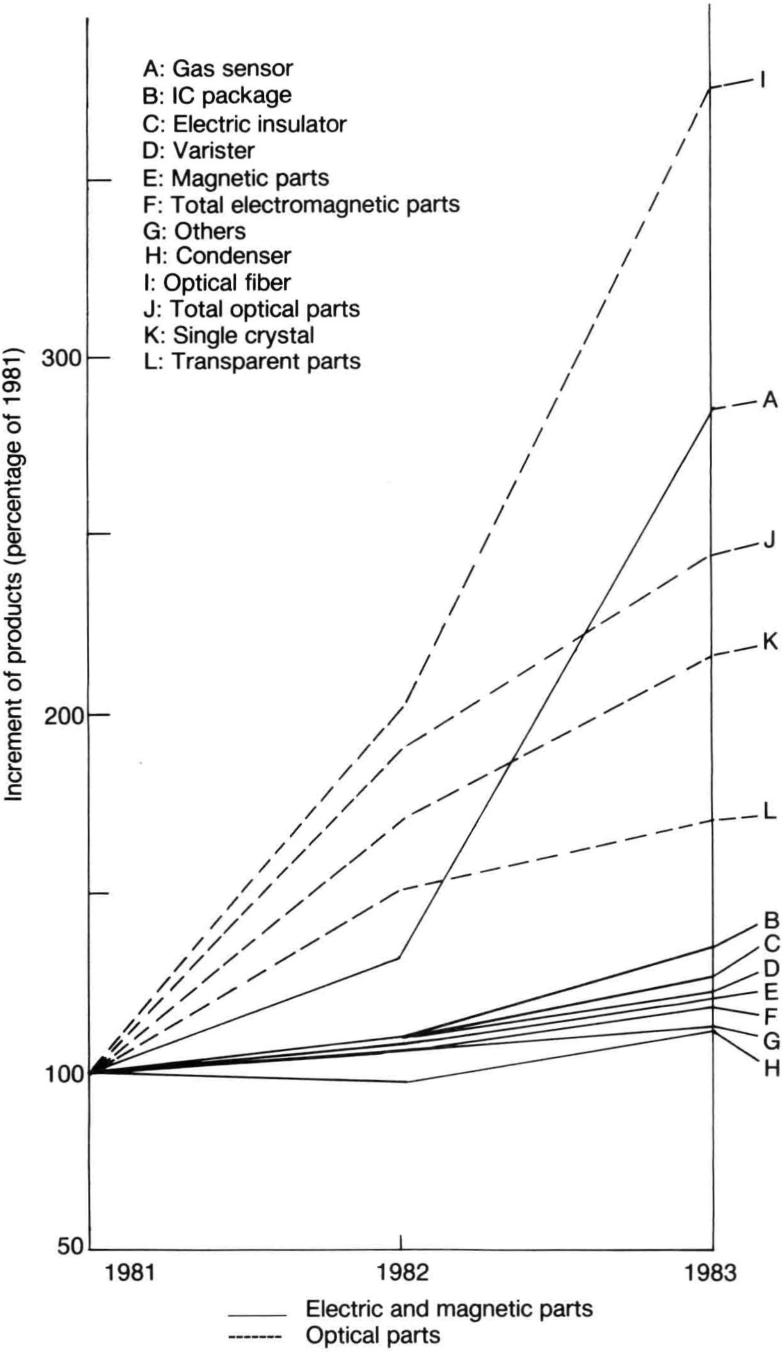

Figure 3 Functional ceramics production trends for 1981 through 1983.

temperature machines, ceramics for precision machinery, and wear-proof and chemical-resistant ceramics. This study is expected to last as long as ten years, during which time three inspections will be carried out.

One of the most attractive areas in structural ceramics being researched in the MITI project is the development of a ceramic engine. There are already many approaches to developing ceramic engines, including the American auto gas turbine (AGT) series and several Japanese types of reciprocating engines and turbines. For reciprocating ceramic engines, the calculated thermal efficiencies from mere adiabatic effects are 32.53% and 40.41% for gasoline and diesel engines, respectively, as against 29.90% and 38.31% for metal engines. These energy gains themselves are not so large, but the ceramic engine has many additional advantages, including high refractoriness and light weight. Further, its total efficiency can be expected to be increased by combining such systems as adiabatic engines and turbochargers. Also, in other fields such as very high-temperature furnaces, high-temperature heat exchangers (made of SiC, for instance) will be greatly beneficial not only in reducing energy consumption but also in producing an extremely elevated temperature source by fuel combustion. These traits will be particularly advantageous in producing high-temperature gas turbines that can be operated without voluminous cooling systems.

Zirconia and alumina are regarded as important for high-temperature as well as high-strength ceramics. It is interesting that household merchandise such as knives and scissors have begun to be made of zirconia and alumina in Japan, while no foreign ceramists have yet thought of such applications. However, these are not just casual Japanese ideas. The world's nations, especially the advanced countries, have begun a significant shift to so-called tertiary industries—that is, the very soft industries. Therefore, the new Japanese fine ceramics industries must reorient toward secondary production.

CONTENTS

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