Glass-Ceramic Technology

Second Edition

Wolfram Höland and George H. Beall

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GLASS-CERAMIC TECHNOLOGY

INTRODUCTION TO THE SECOND EDITION

The aim of the second edition of this reference book is to present the research and development work that has been conducted on glass-ceramic materials since 2002, the year in which the first edition of this book was published. Significant advances have been made since that time in the development of glass-ceramics, which exhibit either special optical properties or exceptional mechanical characteristics, such as high strength and toughness. In this new edition, these development trends are discussed with emphasis on controlled nucleation and crystallization in specific materials systems. In this regard, readers are given a deeper understanding of inorganic solid-state chemistry through the examination of crystalline phase formation reactions. The authors have attached great importance to recording these crystal phase formation processes in close relation to the primary glass phases using a wide variety of analytical methods and to clearly presenting their work. Based on their findings, the properties and special applications of the materials are then introduced. Here, special attention is given to the application of glass-ceramics as materials with special optical properties and biomaterials for dental application. Also, new composite materials, containing glass-ceramics and high-strength polycrystalline ceramics, as well as on new bioactive materials that have been developed to replace bone, are reported.

The second edition of this publication, like the first edition, is the product of a close collaboration between the two authors. While writing their individual sections, they consulted intensively with each other on the different aspects of phase formation, and the development of properties and applications.

W. Höland would like to give special mention to the following people for their scientific discussion on the book project: R. Nesper, F. Krumeich, M. Wörle (all from the Swiss Federal Institute of Technology, Zurich, Switzerland), E. Apel, C. Ritzberger, V. M. Rheinberger (Ivoclar Vivadent AG, Liechtenstein), R. Brow (University Missouri-Rolla, United States), M. Höland (Interstate University of Applied Sciences of Technology Buchs NTB, Switzerland), A. Sakamoto (Nippon Electric Glass Co., Ltd., Japan), J. Deubener (Clausthal University of Technology, Germany), and R. Müller (Federal Institute for Materials Research and Testing, Berlin, Germany). S. Fuchs (South Africa) is thanked for the translation work. C. Ritzberger is specially thanked for his technical experience in the preparation of the second edition of this textbook.

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April 2012

Color versions of figures appearing in this book may be found at ftp://ftp.wiley.com/public/sci_tech_med/glass_ceramic.

INTRODUCTION TO THE FIRST EDITION

Modern science and technology constantly require new materials with special properties to achieve breathtaking innovations. This development centers on the improvement of scientific and technological fabrication and working procedures. That means rendering them faster, economically more favorable, and better in quality. At the same time, new materials are introduced to increase our general quality of life, especially as far as human medicine and dentistry, or our daily life, for example, housekeeping, are concerned.

Among all these new materials, one group plays a very special role: glass-ceramic materials.

They offer the possibility of combining the special properties of conventional sintered ceramics with the distinctive characteristics of glasses. It is, however, possible to develop modern glass-ceramic materials with features unknown thus far in either ceramics or glasses, or in other materials, such as metals or organic polymers. Furthermore, developing glass-ceramics demonstrates the advantage of combining various remarkable properties in one material.

A few examples may illustrate this statement. As will be shown in the book, glass-ceramic materials consist of at least one glass phase and at least one crystal phase. Processing of glass-ceramics is carried out by controlled crystallization of a base glass. The possibility of generating such a base glass bears the advantage of benefiting from the latest technologies in glass processing, such as casting, pressing, rolling, or spinning, which may also be used in the fabrication of glass-ceramics or formation of a sol–gel derived base glass.

By precipitating crystal phases in the base glass, however, new, exceptional characteristics are achieved. Among these, for example, the machineability of glass ceramics resulting from mica crystallization, or the minimum thermal expansion of chinaware, kitchen hot plates, or scientific telescopes as a result of β-quartz-β-spodumene crystallization.

Another new and modern field consists of glass-ceramic materials, used as biomaterials in restorative dentistry or in human medicine. New high-strength, metal-free glass-ceramics will be presented for dental restoration. These are examples that demonstrate the versatility of material development in the field of glass-ceramics. At the same time, however, they clearly indicate how complicated it is to develop such materials and what kind of simultaneous, controlled solid-state processes are required for material development to be beneficial.

The authors of this book intend to make an informative contribution to all those who would like to know more about new glass-ceramic materials and their scientific–technological background or who want to use these materials and benefit from them. It is therefore a book for students, scientists, engineers, and technicians. Furthermore, the monograph is intended to serve as a reference for all those interested in natural or medical science and technology, with special emphasis on glass-ceramics as new materials with new properties.

As a result of this basic idea, the first three chapters, which are (1) "Principles of designing glass ceramic," (2) "Composition systems for glass-ceramic," and (3) "Microstructural control" satisfy the requirements of a scientific–technological textbook. Chapters 1, 2, and 3, in turn, supply in-depth information on the various types of glass-ceramic material. The scientific methods of material development are clearly pointed out, and direct parallels to Chapter 4 on "Applications" can be easily drawn. Therefore, Chapter 4 of the book focuses on the various possibilities of glass-ceramic materials in technical, consumer, optical, medical, dental, electrical, electronic, and architectural applications, as well as uses for coating and soldering. This chapter is arranged like a reference book.

Based on its contents, the present book may be classified somewhere between a technical monograph, textbook, or reference book. It contains elements of all three categories and is thus likely to appeal to a broad readership the world over. As the contents of the book are arranged along various focal points, readers may approach the book in a differentiated manner. For instance, engineers and students of materials science and technology will follow the given structure of the book, beginning at Chapter 1 to read it. By contrast, dentists or dental technicians may want to read Chapter 4 first, where they find details on the application of dental glass-ceramics. Thus, if they want to know more details on the material (microstructure, chemical composition, and crystals), they will read Sections 4.1, 4.2, or 4.3.

The authors carry out their scientific-technological work on two continents, namely America and Europe. Since they are in close contact to scientists of Japan in Asia, the thought arose to analyze and illustrate the field of glass ceramics under the aspect of "glass-ceramic technology" worldwide.

Moreover, the authors, who have worked in the field of development and application of glass-ceramic materials for several years or even decades, have the opportunity to introduce their results to the public. They can, however, also benefit from the results of their colleagues, in close cooperation with other scientists and engineers.

The authors would like to thank the following scientists who helped with this book project by providing technical publications on the topic of glass-ceramic research and development

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HISTORY

Glass-ceramics are ceramic materials formed through the controlled nucleation and crystallization of glass. Glasses are melted, fabricated to shape, and thermally converted to a predominantly crystalline ceramic. The basis of controlled internal crystallization lies in efficient nucleation, which allows the development of fine, randomly oriented grains generally without voids, microcracks, or other porosity. The glass-ceramic process, therefore, is basically a simple thermal process, as illustrated in Fig. H1.

It occurred to Reamur (1739) and to many people since that a dense ceramic made via the crystallization of glass objects would be highly desirable. It was not until about 35 years ago, however, that this idea was consummated. The invention of glass-ceramics took place in the mid-1950s by the famous glass chemist and inventor, Dr. S.D. Stookey. It is useful to examine the sequence of events leading to the discovery of these materials (Table H1).

Dr. Stookey at the time was not primarily interested in ceramics. He was preoccupied in precipitating silver particles in glass in order to achieve a permanent photographic image. He was studying as host glasses lithium silicate compositions because he found he could chemically precipitate silver in alkali silicate glasses, and those containing lithium had the best chemical durability. In order to develop the silver particles, he normally heated glasses previously exposed to ultraviolet light just above their glass transition temperature at around 450°C. One night, the furnace accidentally overheated to 850°C, and, on observation of the thermal recorder, he expected to find a melted pool of glass. Surprisingly, he observed a white material that had not changed shape. He immediately recognized it as a ceramic, evidently produced without distortion from the original glass article. A second srendipitous event then occurred. He dropped the sample accidentally, and it sounded more like metal than glass. He then realized that the ceramic he had produced had unusual strength.

On contemplating the significance of this unplanned experiment, Stookey recalled that lithium aluminosilicate crystals had been reported with very low thermal expansion characteristics; in particular, a phase, β-spodumene, had been described by Hummel (1951) as having a near-zero thermal expansion characteristic. He was well aware of the significance of even moderately low expansion crystals in permitting thermal shock in otherwise fragile ceramics. He realized if he could nucleate these and other low coefficient of thermal expansion phases in the same way as he had lithium disilicate, the discovery would be far more meaningful. Unfortunately, he soon found that silver or other colloidal metals are not effective in nucleation of these aluminosilicate crystals. Here he paused and relied on his personal experience with specialty glasses. He had at one point worked on dense thermometer opals. These are the white glasses that compose the dense, opaque stripe in a common

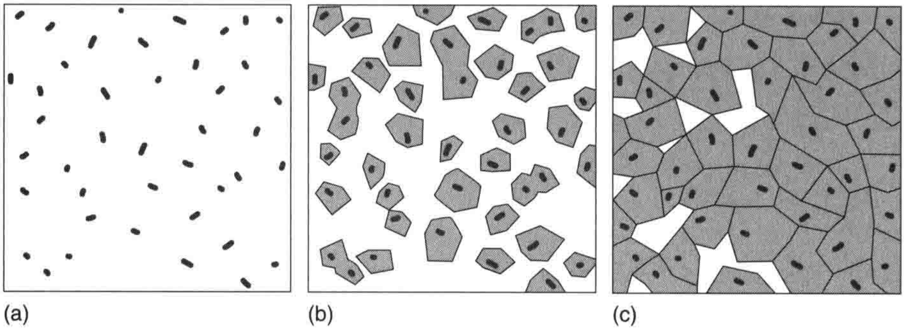


Figure H1 From glass to glass-ceramic. (a) Nuclei formation, (b) crystal growth on nuclei, and (c) glass-ceramic microstructure.

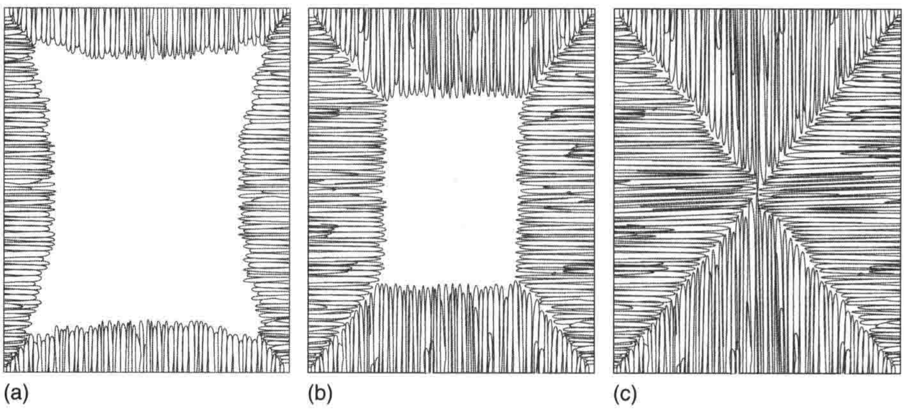
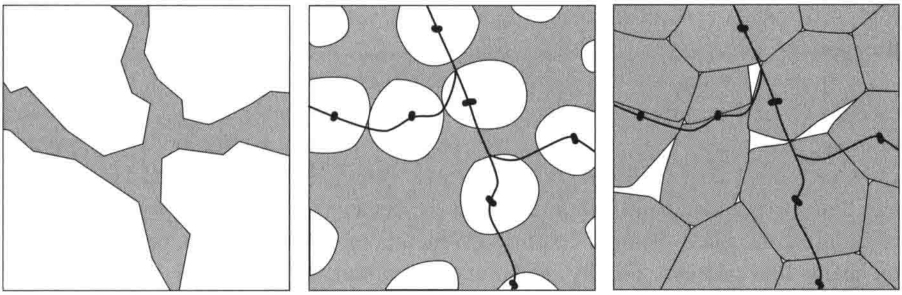


Figure H2 Crystallization of glass without internal nucleation.

thermometer. Historically, this effect had been developed by precipitation of crystals of high refractive index, such as zinc sulfide or titania. He, therefore, tried adding titania as a nucleating agent in aluminosilicate glasses and discovered it to be amazingly effective. Strong and thermal shock-resistant glass-ceramics were then developed commercially within a year or two of this work with well-known products, such as rocket nose cones and Corning Ware® cookware resulting (Stookey, 1959).

In summary, a broad materials advance had been achieved from a mixture of serendipitous events controlled by chance and good exploratory research related to a practical concept, albeit unrelated to a specific vision of any of the eventual products. Knowledge of the literature, good observation skills, and deductive reasoning were clearly evident in allowing the chance events to bear fruit.

Without the internal nucleation process as a precursor to crystallization, devitrification is initiated at lower energy surface sites. As Reamur was painfully aware, the result is an ice cube-like structure (Fig. H2), where the surface-oriented crystals



(a) (b) (c)

Figure H3 Glass-ceramics from powdered glass. (a) Powdered glass compact, (b) densification and incipient crystallization, and (c) frit-derived glass-ceramic.

TABLE H1 Invention of glass-ceramics (S.D. Stookey, 1950s)

- Photosensitive silver precipitation in Li_2O–SiO_2 glass; furnace *overheats*; $Li_2Si_2O_5$ crystallizes on Ag nuclei; first glass-ceramic
- Sample *accidentally dropped*; unusual strength
- Near-zero thermal expansion crystal phases described in Li_2O–Al_2O_3–SiO_2 system (Hummel, Roy)
- TiO_2 tried as nucleation agent based on its observed precipitation in *dense thermometer opals*
- Aluminosilicate glass-ceramic (e.g., Corning Ware®) developed

meet in a plane of weakness. The flow of the uncrystallized core glass in response to changes in bulk density during crystallization commonly forces the original shape to undergo grotesque distortions. On the other hand, because crystallization can occur uniformly and at high viscosities, internally nucleated glasses can undergo the transformation from glass to ceramic with little or no deviation from the original shape.

To consider the advantages of glass-ceramics over their parent glasses, one must consider the unique features of crystals, beginning with their ordered structure. When crystals meet, structural discontinuities or grain boundaries are produced. Unlike glasses, crystals also have discrete structural plans that may cause deflection, branching, or splintering of cracks. Thus, the presence of cleavage planes and grain boundaries serves to act as an impediment for fracture propagation. This accounts for the better mechanical reliability of finely crystallized glasses. In addition, the spectrum of properties in crystals is very broad compared with that of glasses. Thus, some crystals may have extremely low or even negative thermal expansion behavior. Others, like sapphire, may be harder than any glass, and crystals like mica might be extremely soft. Certain crystalline families also may have unusual luminescent, dielectric, or magnetic properties. Some are semiconducting or even, as recent advances attest, may be superconducting at liquid nitrogen temperatures. In addition, if crystals can be oriented, polar properties like piezoelectricity or optical polarization may be induced.

In recent years, another method of manufacture of glass-ceramics has proven technically and commercially viable. This involves the sintering and crystallization of powdered glass. This approach has certain advantages over body-crystallized glass-ceramics. First, traditional glass-ceramic processes may be used, for example, slip casting, pressing, and extruding. Second, because of the high flow rates before crystallization, glass-ceramic coatings on metals or other ceramics may be applied by using this process. Finally, and most important, is the ability to use surface imperfections in quenched frit as nucleation sites. This process typically involves milling a quenched glass into fine 3–15-μm particle diameter particulate. This powder is then formed by conventional ceramming called forming techniques in viscous sintering to full density just before the crystallization process is completed. Figure H3 shows transformation of a powdered glass compact (Fig. H3a) to a dense sintered glass with some surface nucleation sites (Fig. H3b) and finally to a highly crystalline frit derived glass-ceramic (Fig. H3c). Note the similarity in structure between the internally nucleated glass-ceramic in Fig. H1c. The first commercial exploitation of frit-derived glass-ceramics was the devitrifying frit solder glasses for sealing television bulbs. Recently, the technology has been applied to cofired, multilayer substrates for electronic packaging.

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