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陶瓷新型胶态成型工艺

Novel Colloidal Forming of Ceramics

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About Authors

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Born in 1937, graduated from Tsinghua University in 1962. He has been engaging in inorganic nonmetallic material teaching and research for many years. He was the visiting scholar at the Department of Materials Science and Engineering in the University of Michigan in U.S.A., the research scientist at the material center of Massachusetts Institute of Technology in America, the visiting professor at the Department of Materials in Swiss Federal Institute of Technology (ETH Zurich), and also carried out a cooperative research with the University of Monash in Australia. His research interests include the composing, structure and performance of the advanced ceramic, as well as the preparation of high performance ceramic and the strengthening mechanism. He has won many top honors, including the second class National Technology Invention Award for a research program by State Council of China and "Science and Technology Advancement Prize" for other nine programs awarded by the Ministry of Education and the government of Beijing, Fujian Province respectively. He has delivered more than 400 papers, got 25 state patents for invention, published 14 teaching materials, text book, handbook etc. He was rewarded a national excellent text book and the first class award of excellent text book for building materials. He also was rewarded for the excellent teacher of Beijing, advanced person of the State Plan for Development of Basic Research and the winner of special government allowance.

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Born in 1966, graduated from Beijing Institute of Technology in 1987, graduated and got the master degree from North University of China (NUC) in 1990, got the doctor degree from Tsinghua University in 1996. He had the post-doctoral experience at Department of Materials in Swiss Federal Institute of Technology (ETH-Zurich) from 1999 to 2000. He became a full professor in Tsinghua University in 2004, and had the position of special-engaged professor and director of laboratory of advanced ceramics in NUC since 2006.

Research fields include: structured ceramics, ceramic matrix composites, colloidal forming technology of ceramics and laser green machining of ceramics. He had won some top honors, including the second class prize of National Technology Invention for a research program by State Council of China, and "Science and Technology Advancement Prize" for other three programs awarded by the Ministry of Education and the government of Beijing respectively. He has delivered more than 100 papers, and got 30 state patents for invention.

Introduction

In ancient times, ceramic vessels or crafts were usually manufactured using clay-based natural raw materials. It is well known that the mud mixed clay with water had a good plasticity, and can be easily processed into various products with different shapes. However, their forming techniques used earlier were mainly manual procedures. So, to a large extent, the forming of ceramic wares was just as a kind of skill or workmanship. By the 1960s, new ceramic materials had already developed into an independent scientific system. At the same time, the raw materials that were used to manufacture ceramics began to transition from the clay-based system to the one with accurate chemical composition. In particular, for preparing high-performance ceramics, the synthetic chemical raw materials, such as Al_2O_3, ZrO_2, Si_3N_4, SiC and so on, were mainly used. These ceramics had excellent properties because of their structure characteristics of covalent bond and ionic bond, and were widely considered as candidate materials in many fields requiring high-temperature resistant, wear-resistant, and corrosion resistant substances. It had been predicted that such materials would be developed rapidly, and various new types of materials with excellent properties would be explored.

By the late 1970s, the emergence of the worldwide oil crisis caused many developed countries led by America and Japan to draft national development plans for high-temperature structural ceramic materials used in the field of internal combustion engine especially the automobile engines. With excellent properties such as resistance to high temperature, wear, and corrosion, the high-performance ceramics were acted as the optimal material for non-water cooling and adiabatic ceramic engine parts. The forming technique of ceramic was also been ranked the important research topics.

During the period of the "7th Five-Year Plan" (1986 – 1990) and "8th Five-Year Plan" (1991 – 1995) in China, around the key components of ceramic insulation engines, an in-depth research on the ceramic injection molding, extrusion molding, slip casting, and pressure filtration was done. Moreover, a few engine parts samples with high performance were prepared. However, because of the high cost, poor performance repeatability, and low yield, the process of industrialization of high-performance ceramics was greatly restricted. After years of research and development, there was a growing recognition as the key technology for forming high-performance ceramic materials and parts. The forming technique is not only the precondition for materials design and formulation, but also the important factor in reducing the manufacturing costs, improving the yield and the performance repeatability of the products. Simultaneously, several research booms were set off around the new forming technique of ceramics at home and abroad. During the period of the "9th Five-Year Plan" (1996 – 2000), in order to achieve high-tech ceramic industrialization as soon as possible, the ceramic forming technique with high performance and low cost was granted special funds from the "863 Program" (the National High-Tech Research and Development Program of China).

Along with the research upsurge in the field of ceramic engines, there was also considerable interest in the field of the injection molding of ceramics. On the basis of the theory of plastic injection molding, thermoplastic, thermosetting, and water-soluble organic compounds were used as binders, and then mixed with ceramic powder to prepare a suspension with high solid loading. In addition, ceramic parts with high size precision and complex shape can be prepared by injection molding. It is suitable for automotive and large-scale production. After several decades, owing to in-depth studies on ceramic injection molding, it developed into an integrated science and technology involving rheology, the dynamic molding process of injection suspension, and thermal degradation of organic compounds as well as other interdisciplinary technology. However, some problems which were caused by organic enrichment or particle rearrangement were exposed during the time and energy consuming process of de-bindering, such as poor uniformity and easy cracking. Therefore, the de-bindering was considered as the key issue to be solved, and the solution to lower the organic content gradually became an important research topic. In order to simplify the process of de-bindering, the low pressure injection molding with some small molecular organics was paid more attention.

After the 1990s, quickset injection molding was invented by B. E. Novich of the U.S.A. The pore fluid was used as a carrier in the process, its volume did not change with temperature. After the suspension was injected into the container, the carrier was sublimated, and then the green body was solidified by controlling the temperature and pressure. Because of avoiding the polymer organic carrier with large molecule, the problem of organic de-bindering was solved ingeniously. At present, due to those significant advantages such as high automation and good size precision, the injection molding continues to be highly used and is considered to be a highly competitive forming process.

In the mid-1980s, in order to avoid the difficulty of de-bindering in the injection molding, which was caused by the large number of organic binders, the traditional slip casting attracted more interests, as it involved less organic content and low cost. Moreover, the operation and control were easy in this method. However, because of the green body with low green density and poor strength, it was not suitable for high reliability ceramics. On the basis of traditional slip casting, the pressure filtration and centrifugal casting techniques were developed thereafter. The green body's density and strength were improved by applied pressure and centrifugal force, and at the same time the complicated de-bindering process was avoided. However, such processes were also unable to meet the production of the green bodies with high reliability and high performance due to poor uniformity of the green bodies.

After the 1990s, in order to improve the uniformity and reliability of ceramic bodies, the forming *in-situ* techniques, such as gel-casting, temperature induced flocculation, colloidal vibration casting and direct coagulation casting were developed. The *in-situ* solidification process is highly regarded because it is the precondition to ensure the uniformity and is an important way to improve the reliability of ceramics.

Gel-casting, a novel colloidal forming technology of ceramics, was first invented by Oak Ridge National Laboratory (ORNL), U.S.A., in 1990. In the gel-casting process, about 2 – 4 wt% acrylamide monomer is added into the ceramic suspension, and then it polymerizes *in-situ* by the interaction of catalysts and initiators. Furthermore, the drying process should take place at room temperature and high humidity for a long time, otherwise the green bodies would easily crack. In addition, the degree of automation and industrialization of the gel-casting process is poor when compared to the injection molding. The ceramic bodies prepared by gel-casting have the obvious advantages of high strength and excellent machinability. Thus, some ceramic parts with complex shape, or that are difficult to be demoulded, just like inside screw, can be passed through green body machining after drying to achieve the required shape and precision. As a kind of brittle and difficult-to-machine material, it is very important, even necessary for the bodies to be machined partly, which also provides people a very good idea.

Temperature-induced flocculation was developed by L. Bergstrom at the Institute of Surface Chemistry of Stockholm University, Sweden, in 1993. A special amphoteric polyester surfactant or dispersant changing with temperature is introduced into the concentrated suspension to make particles to disperse, one end of the dispersant is adsorbed on the particle surface, the other end goes inside the solvent. As the temperature is reduced, the solubility of dispersant declines and the function of dispersion fails and then the suspension is flocculated *in-situ*. The outstanding advantage of the method is the recycling of the unqualified green bodies, but it is restricted to use such dispersant for the different ceramic system.

Colloidal vibration casting was first developed by F. F. Lange at the California University in Santa Babara, U.S.A., in 1993. The prepared dilute suspension (20 – 30 vol%) with high ionic concentration will be pressure-filtered or centrifuged to obtain the green body with high solid loading, which is in the solid state under static conditions but is in the fluid state if certain external force (such as vibration) are applied. Then, the suspension will solidify *in-situ* under static conditions after it being poured. The advantage is the use of the thixotropic property when the concentrated suspension has a high ionic strength. Moreover, the concentrated suspension don't need to prepare with high solid loading. However, the green bodies have poor strength and are prone to cracking and deformation.

Direct coagulation casting was invented by the research team of Gauckler at the Swiss Federal Institute of Technology in Zurich, Switzerland in 1994. In this method, first, a biological enzyme and a substrate are introduced into the ceramic concentrated suspensions at low temperature (~5℃). At this time the enzyme is in the inactivated state and does not almost react with the substrate. Then, the temperature of the suspension rises from 0 – 5℃ to 20 – 40℃, and the enzyme is activated and reacts with substrate. By adjusting the pH to the isoelectric point or by increasing ionic strength, the suspensions is coagulated *in- situ*. This method results in wet bodies with enough strength to be demoulded. In the process, it is necessary that the solid loading of suspension is more than 50 vol%, but the strength of the wet green body is low. However, the body is extremely uniform and does not contain any organic binder. Thus, it is suitable for preparing high reliability ceramics, for which the Weibull modulus can reach 40.

Thus, after the 1990s, the research on the *in-situ* forming technique had become a new hotspot in the field of high-performance ceramics. It is gradually realized that the forming technique take a very important position in the study of ceramic materials, and that the industrialization process of high-performance ceramics would be promoted greatly through the in-depth study on the forming technique and its basic theory. In the mid-1980s, the injection molding and pressure filtration had been studied at Tsinghua University in China. After the 1990s, the study of gel-casting and direct coagulation casting had been progressed significantly, especially with the invention of the novel injection molding for water-based nonplastic slurry of ceramic, also called as colloidal injection molding. A colloidal injection molding machine was also developed. The development of gel-tape-casting process and gel-casting with low toxicity system was studied in detail in about five years. Recently, freeze-gel-casting technique and colloidal forming of ultra-light and high strength porous ceramic have been invented, which further enrich the theory and technique of ceramic forming. The industrialization process of high-performance ceramics is also being promoted greatly. In China, other universities and institutes such as Shanghai Institute of Ceramics of Chinese Academy of Sciences and Tianjin University, etc., are doing the similar research. The key technology and development trends, regarding the colloidal forming of ceramics, include the following aspects:

(1) The preparation of a concentrated suspension with low viscosity and high solid loading is the precondition to guarantee the density, uniformity, and strength of the green bodies. With high density, the shrinkage of the green bodies can be

decreased in drying, and the deformation and cracking can be avoided in the sintering process. Therefore, the foundation of colloidal forming is to prepare the suspension with high solid loading.

(2) The *in-situ* consolidation technique. In a sense, a new consolidation technique of suspension means a new forming process. It is very important for colloidal forming to look for a new solidification method of suspension. For *in-situ* forming, the relative position of particles does not change during the solidification of suspension. It is a necessary condition to guarantee the body uniformity, which is also a key factor to improve the reliability of ceramic materials. Currently, the development of an *in-situ* consolidation technique requires the suspension to contain few or no organic substances. By varying the charged and dispersant characteristic between colloidal particles, the viscosity of suspension is increased and this leads to *in-situ* solidification of the green bodies. At the same time, with the enough strength to be demoulded, the ceramic green bodies can be easily transported during a large scale production.

(3) It is very important to avoid the residual stress in green body by using the colloidal forming. Normally, there is no shrinkage during forming suspension to green body, and no residual stress in green body. So we believe that the colloidal forming without shrinkage will become an important trend in the next 10 – 20 years.

(4) Near net size forming. Ceramics are the hard-machined material with high hardness and brittleness. The sintered bodies should be close to the actual size of the final parts in order to decrease machining of ceramics.

The preparation process of high-performance ceramic materials and parts is very important for development and application of ceramics. It involves the preparation of high-performance ceramic powders, and the forming and sintering processes. The quality of green and sintered body is directly impacted by the quality of the powders because the rheological behaviors and solid loading of concentrated suspension are directly determined by the properties of the powder during colloidal forming. Moreover, the quality of green bodies guarantees the quality of sintered body. The preparation of powders, and the forming and sintering of ceramics are mutual constraints and complementary. However, according to the current development of ceramic forming, the forming process, which plays an important role in the preparation process of ceramic materials and is related with the industrialization and scale of production, is the critical step to guarantee the performance reliability and repeatability as well as the yield of ceramics. Hence, it is of great significance to research on the forming technique of ceramics with low cost and high reliability, and it will promote the industrialization of high-performance ceramics in the world. This is not only the requirement of governments around the world and of industries, but also the urgent need of ceramic scientists.

To sum up, the green bodies prepared by an ideal forming process should have a good uniformity, a high green density, enough strength to be demoulded, and no residual internal stress. The ceramic materials with high performance can be obtained by using the forming process, the homogeneous of shrinkage would be guaranteed and deformation avoided during the sintering process. In order to meet the above requirements, the forming process from a technical perspective should have the following characteristics:

(1) Adding no or as few as possible organic polymers (0.1 – 4 wt%).

(2) The solid loading of suspension is more than 55 vol%.

(3) The solidification of suspension is a rapid and *in-situ* technology.

(4) The suspension has no shrinkage and internal stress during the transformation from liquid to solid state.

(5) A kind of near net size forming process.

The first point is to avoid the problem of debindering. The second point is to improve the density and the strength of the green bodies. The third point is to guarantee the uniformity and the dimensional accuracy of the green bodies. The fourth point is to avoid deformation and cracking of the green bodies during burn-out and sintering, in order to improve the reliability. The fifth point is to guarantee the dimensional accuracy of sintered products, so that there is no or less machining.

There are seven chapters in the book. The main contents involve our research achievements and developments in two decades. Recent international research results in the field of ceramic forming are also introduced. Finally, the basic problems and the future development trends of forming process are proposed and discussed in detail.

The book writing was completed by Yong Huang and Jinlong Yang.

It should be noted that professor Zhipeng Xie and his graduate students achieve the excellent results in the field of colloidal forming process, which enriched the content of this book. Meanwhile he was also personally involved in the compilation and modification of Chapter 3 in this book. Thus we are appreciated his positive contribution for the publication of this book.

Besides Prof. Xie, Xiaoqing Xi, Tian Ma and Yali Wang helped to compile and check for some chapters of the book. At the writing period of this book, Dr. Tao Zhang (Kingston University, United Kingdom), Dr. Hui-rong Le (the United Kingdom Dundee University), Chang-an Wang, Yang Sun, Liguo Ma et al. proposed some revision opinions to some chapters of the book. The special thanks are given to them for their support and help during finishing this book.

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Contents

Chapter 1 Aqueous Colloidal Injection Molding of Ceramics Based on Gelation

Abstract In this chapter, an aqueous colloidal injection molding of ceramics (CIMC) which is based on gelation of monomer polymerization, like a reactive injection molding of double-slurry of polyester, is discussed systematically. The solidification mechanism is based on gelation of monomer polymerization. It was found that pressure can induce the polymerization of monomer. The gelation time can be effectively controlled by temperature and pressure. The testing equipment of gel point was developed and used to test gel reaction of monomer in suspension under different pressures. A machine for ceramic colloidal injection molding was developed. The copper was proved to accelerate the polymerization of monomer. Therefore, the copper parts are forbidden for use in a CIMC machine.

Keywords gel-casting, injection molding, colloidal injection molding, pressure induced forming, fast mixing with double suspensions, ceramic slurry

High-performance ceramics are becoming increasingly more important in several fields, such as spaceflight, energy, mechanics, and bio-techniques. But the high cost and low reliability have prevented high-performance ceramics to be utilized on a large scale until now. To solve this problem, more attention is being paid to the forming process of ceramics. In the industrialization of high-performance ceramics, forming has become a bottleneck and needs to solve. Colloidal forming is an important forming technique. It includes slip casting, tape casting, direct coagulation casting (DCC), injection molding, gel-casting and so on. Among these techniques, gel-casting and injection molding are considered the two possible solutions to address the industrialization of high-performance ceramics. Though they both have many advantages, there are still several problems to be solved in the industrialization process.

Gel-casting is a new ceramic forming technique that is generating worldwide attention. The process is based on the casting of slurry, containing powder, water, and water-soluble organic monomers. After casting, the mixture is then polymerized to form gelled parts. Drying, burning out and sintering complete the manufacturing process. The process is generic and can be used for a wide range of ceramic and metallic powders. It is a suitable technique for the fabrication of near net shape prototypes or small series using cheap moulds. In contrast with slip casting, gelled parts are more homogeneous and have a much higher green strength.

Gelcast parts contain only a low percent of organic components, thereby making binder removal much less critical compared to injection molding. The advantages of gel-casting can be summarized as follows:

(1) Capability of producing complex parts like injection molding;

(2) Ease of implementation owing to its similarity with other well-established processes like slip casting;

(3) Low capital equipment cost;

(4) Possibility to use low-cost mould materials;

(5) Capability of implementation for mass production;

(6) High green strength;

(7) Excellent green machinability that allows machining much finer details that in cold static pressing (CIP) parts;

(8) Highly homogeneous material properties;

(9) Low organic content that translates into easy binder removal;

(10) Generic method applicable for both ceramic and metal powders.

Meanwhile, there are still some disadvantages that make it difficult to realize the industrialization by gel-casting. Most important of all, low automation prevents gel-casting from being used in the industrialization of high-performance ceramics (Omatete O. O., et al., 1991; Gilissen R., et al., 2000).

Injection molding, however, has been used in the ceramic industry for several decades for its high automation. Ceramic injection molding is a well-established shaping technique, which involves the mixing of ceramic powder with a large concentration of a melt polymer (up to 50 – 60 vol%). The carrier polymer provides very high viscosity, and so very high pressures ((150 ± 10) MPa) and temperatures ((200 ± 120)℃) are needed for injection. In addition to the high cost derived from the use of organics, the major problem arises from the debindering step that can easily lead to defects and failure of the sintered body. In the preparation of products with complex shape and big cross section, the problem is more obvious. These disadvantages prevent injection molding from being used in the industrialization of high-performance ceramics (Novak S., et al., 2000; Wei Wen-Cheng J., et al., 2000; Liu D. M., 1999; Krug S., et al., 2000).

The aim of this study is to develop a new forming technique to meet the needs of industrialization. The new technique is called colloidal injection molding of ceramics (CIMC).

1.1 Colloidal Injection Molding

1.1.1 The Concept of CIMC

Traditional injection molding can be used to form complex ceramic parts with high-dimension precision, so that it can be applied to realize the automation of