High-Performance Structural Ceramics: Powders and Components

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Abstract

High-performance ceramics have attracted much interest during the last decade, but a broad market introduction has not taken place so far due to the inherent disadvantages of ceramic components in applications with high mechanical loadings. The high brittleness and the low reliability as compared to metals, as well as the high production costs are severe obstacles in an area like the automotive engine. Typical defects of ceramic components may be introduced by the powders themselves, but in a like manner, sources of defects also lie in the forming and the densification of the components. The production technologies used for high-performance ceramics are mostly the same that are applied in traditional ceramics. It is demonstrated exemplarily for the materials silicon carbide, zirconia, alumina and silicon nitride, exactly what the main sources of defects are and how they could be avoided. From this, the desired powder properties can be derived. It is expected that improvements in powder processing and forming technologies will improve the reliability of ceramic components and lower the costs, thus leading to the remarkable market growth which has been predicted for more than ten years.

1. Introduction

Components in high-performance ceramics are exclusively made from synthetic powders in order to avoid the deviations in properties typical for natural raw materials. The field of high-performance ceramics can be subdivided into two main areas of application:

- structural ceramics
- electronic ceramics

Structural applications are characterized by high mechanical, thermal and abrasive loading, whereas electronic applications make use of the electrical properties of ceramic materials, which can be either active or passive functions. Table 1 shows the materials which are used in high-performance ceramics with their main field of applications. The materials alumina ($\text{Al}_2\text{O}_3$), silicon carbide ($\text{SiC}$), silicon nitride ($\text{Si}_3\text{N}_4$), and zirconia ($\text{ZrO}_2$) to a lesser extent are the candidates with the highest potential in the future. Today, electronic ceramics have reached a much higher market penetration than structural ceramics. The reason for this lies in the low reliability of structural components which is not only due to unsuitable design, but also due to real existing imperfections in the whole manufacturing process of powders and components. The presented article concentrates on structural ceramics and possible improvements with respect to technical performance and costs.

Table 1: Powders for high-performance ceramics

<table>
<thead>
<tr>
<th>Material</th>
<th>Application</th>
<th>Structural Ceramics</th>
<th>Electronic active</th>
<th>Electronic passive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium - nitride</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>- oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- silicates (Mullite)</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>- titanate</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Barium - titanate</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Lead - (Lanthan-) zirconium-titanate (PZT/PLZT)</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Boron - carbide</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Silicon - carbide</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Titanium - boride</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Zirconium - dioxide</td>
<td></td>
<td>×</td>
<td>×</td>
<td>×</td>
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</tbody>
</table>

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2. Properties of ceramics and related problems

In comparison with the conventional construction materials such as metals and polymers, ceramics show some considerable advantages:
- low density compared to metals
- high hardness
- high thermal and chemical stability
- strength at very high temperatures

On the other hand, severe disadvantages have to be considered:
- low strength at ambient temperature
- high brittleness
- high costs (for powders and components)

The low reliability of ceramics is caused by the brittle fracture behaviour and a wide range of strength values, expressed by a low Weibull modulus. Whereas the brittleness is an intrinsic property of a certain material, the distribution of strength values is correlated directly to the distribution of flaw sizes, as postulated by Griffith [1] in his theory of rupture. This correlation is shown in Fig. 1, where the strength values are plotted versus the critical flaw size with the fracture toughness $K_{IC}$ (reverse of brittleness) as a parameter. The values for ceramics vary between 2 and 12 MPa m$^{1/2}$, whereas a high-toughness-steel reaches up to 200 MPa m$^{1/2}$, which clearly demonstrates the brittleness of ceramics. In order to achieve a required strength level in a given material, only a maximum critical defect size can be tolerated. This can exemplarily be explained for Al$_2$O$_3$ and ZrO$_2$; if a minimum strength level of 500 MPa is required, the tolerable flow size in an alumina ceramic component is 32 μm ($K_{IC} = 3.5$ MPa m$^{1/2}$), whereas in zirconia ($K_{IC} = 10$ MPa m$^{1/2}$) the defect size might be as large as 250 μm.

The above-mentioned example clearly indicates that only two ways of improving the reliability of ceramic components are possible: 1. increasing the fracture toughness and/or 2. increasing the Weibull modulus by reducing the flaw sizes or rather the width of the flaw size distribution.

Possible improvements of the fracture toughness by incorporating a second phase into the matrix material, as described by Nihara [2] for the well-known nano composite ceramics, for example, shall not be discussed in detail in this paper. Improving the strength of ceramic components requires a reduction of flaw sizes. Most of the observed defects can be explained in well-defined terms and are subdivided into three different populations as indicated in Fig. 2. The relative frequency of defects is shown as a function of the defect size. Although the size ranges of the different flaw populations strongly overlap, this schematic view allows conclusions to be drawn about the origin of the respective defect. The kind of defect, the process step in which the defect occurs and the reasons are summarized in Table 2. The underlinings show that powder synthesis and preparation make a considerable contribution to the entirety of defects.

3. Manufacturing of ceramic components as source of defects

In order to better understand the existing problems of structural ceramics, it is necessary to examine the different steps of ceramic processing which are shown in Fig. 3. The process as a whole is quite similar to the manufacturing of traditional ceramics such as tableware, tiles or sanitary ware, except the powder production. Today, the submicron powders Al$_2$O$_3$, SiC, Si$_3$N$_4$ and ZrO$_2$ are mostly produced by...
Table 2 Typical defects of ceramics

<table>
<thead>
<tr>
<th>Kind of defect</th>
<th>Processing step</th>
<th>Origin of defect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface defects</td>
<td>finishing</td>
<td>mechanical loading too high</td>
</tr>
<tr>
<td></td>
<td>green machining</td>
<td>forming tools with defects</td>
</tr>
<tr>
<td></td>
<td>shape forming</td>
<td></td>
</tr>
<tr>
<td>Contaminations</td>
<td>powder synthesis</td>
<td>open systems</td>
</tr>
<tr>
<td></td>
<td>powder preparation</td>
<td>insufficient cleaning</td>
</tr>
<tr>
<td></td>
<td>shape forming</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>powder synthesis</td>
<td>insufficient energy input</td>
</tr>
<tr>
<td></td>
<td>powder preparation</td>
<td>during mixing/homogenizing</td>
</tr>
<tr>
<td></td>
<td>shape forming</td>
<td>hard agglomerates</td>
</tr>
<tr>
<td></td>
<td>sintering process</td>
<td>bad flowing properties</td>
</tr>
<tr>
<td></td>
<td>powder synthesis</td>
<td>oversized grains in the powder</td>
</tr>
<tr>
<td></td>
<td>powder preparation</td>
<td>non-homogeneous distribution of</td>
</tr>
<tr>
<td></td>
<td>sintering process</td>
<td>sintering aids</td>
</tr>
<tr>
<td>Broad distribution of</td>
<td></td>
<td>sintering temperature too high</td>
</tr>
<tr>
<td>crystalite sizes</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comminution of coarser materials which are primarily made for abrasive, refractory or metallurgical applications. Particle growth methods such as precipitation followed by crystallization or gas-phase reactions are used to a lesser extent for high purity aluminas and ZrO₂-TZP-powders, and the latter in an experimental stage for Si₃N₄ and SiC. But also with those so-called more advanced processes for powder synthesis, the problems in powder processing remain the same. Complete deagglomeration and homogeneous mixing of the inorganic and organic additives are of utmost importance. The main sources of defects, which cannot be corrected in the subsequent processing steps, lie in the powder production and preparation.

In the following, some examples of the link between flaw type and processing step are accentuated from the summarizing description of Table 2. Surface defects may originate during finishing, green machining or by the forming tools directly. External contaminations are not possible after the forming process has been finished, but they can easily occur during the powder production and preparation. Inhomogeneities in density can be introduced in the forming and the densification process, but they can also be attributed to an inadequate powder preparation process. Chemical non-homogeneities are due only to incomplete mixing and homogenizing, which might be caused by insufficient mixing intensity and time or indestructible aggregates in the powder. The existence of large grains in the microstructure of the densified ceramic material is mainly due to unsuitable powder qualities and/or a densification process which is not optimally adjusted in terms of temperature and time.

4. Typical defects and possible solutions

This section focuses on the effect of powder production and preparation on the final microstructure. The experimental work has been conducted on the materials silicon carbide, zirconia, alumina and silicon nitride.

4.1 Silicon carbide

Two submicron SiC powders (Fig. 4) have been mixed with the sintering aids boron carbide, carbon and the organic additives. After axial pressing at 200 MPa, the materials were densified under identical conditions (2130°C in argon atmosphere) to reach a final density of > 97% of the theoretical density. Powder A, with a narrow particle size distribution, results in a fine grained microstructure, whereas powder B, which contains 5% of larger grains between 2 and 6μm, leads to a microstructure with exaggerated grain growth. Some large crystallites of approximately 150μm in size will substantially reduce the strength of such a component.
Besides the coarse particles, detectable by the usual methods and shown in curve B of Fig. 4, the powders usually contain very small quantities of oversized grains which are not accessible to an optical measuring method. Using instead ultrasonic wet screening with round sieve openings of 5 μm reveals that the very small amount of 0.06 wt. % of large single crystals or hard agglomerates are present also in the powder A. Fig. 5 shows a SEM picture of the residue on a 5μm sieve. The influence of this kind of oversized grain on the reliability of SiC ceramics is demonstrated in Fig. 6, where the strength distributions of components obtained by two different powders are shown. In case 1, a commercially available SiC powder leads to a mean strength value of 380 MPa with a Weibull modulus of 5. If the oversized grains > 2μm are eliminated, the strength can be improved to 570 MPa and the Weibull modulus to 15, clearly demonstrating the scope of possible improvement.

As mentioned earlier in this paper, SiC powders have to be mixed with sintering additives in order to successfully allow pressureless sintering. The mixing process is difficult, because materials with

Fig. 4 Exaggerated grain growth in sintered SiC

Fig. 5 Oversized grains in SiC powder

Fig. 6 Influence of oversized grains on the strength distribution of SiC ceramics
extremely different physical/chemical properties such as density, specific surface area and wettability must be homogenized. Additionally, the quantities to be homogenized may differ by orders of magnitude. The result of a poor mixing process can be seen in Fig. 7, where an agglomerate consisting of mainly carbon and boron carbide with a diameter of 150µm results in a very porous area of the microstructure, thus acting as the fracture origin. Chemical homogeneity can be reached by intensive mixing or milling. Adjusting the surface chemical properties of the single components in the mixture is also of great importance.

Fig. 7 Chemical non-homogeneity in sintered SiC

4.2 Zirconia

Two commercially available co-precipitated ZrO₂ powders with 3 mol percent yttria each and a primary crystallite size of 40 nm have been pressed under identical conditions. The pore size distributions of the green compacts were measured by a mercury porosimeter and the sintering behaviour was characterized by densification in a dilatometer. The results are presented in Fig. 8 [3]. The powder L has a very narrow, monomodal pore size distribution with a mean value of slightly above 10 nm (upper left part). The corresponding curve of the sintering rate (upper right part) during heating also shows a monomodal shape and the shrinkage is finalized at 1600°C. In contrast to this, powder C has a bimodal pore size distribution due to hard agglomerates of the primary crystals (lower left part). The corresponding sintering curve (lower right part) shows that the smaller pores of 10 nm are eliminated at the same temperature found for powder L, but that the larger pores in the case of powder C require a much higher temperature of nearly 1800°C for full densification. As a result of the high sintering temperature, additional grain growth occurs with the negative effect on the strength behaviour already mentioned in the case of SiC.

4.3 Alumina

A low-soda alumina powder with a specific surface area of 8 m²/g was mixed with the organic additives, spray dried, isostatically pressed at 100 MPa and sintered. The results of this processing are shown in figure 9, parts a), b) and c). Part a) gives an impression of the powder after spray granulation, b) shows a cross-section of the green body and c) of the sintered material. Large pores up to more than 100µm can be found. The reasons for this can either be hard granules which are not deformed or destroyed during the pressing step or collapsed hollow granules. Optimizing the organic additives and the conditions for spray granulation leads to the result shown in part d) of Fig 9. The density could be increased from 3.91 g/cm³ to 3.97 g/cm³ and the maximum pore sizes are smaller than 10µm. In this case, the two main sources of pores, hollow granules and large triple points in the green compact, can be avoided by increased solids content of the slurry prior to spray drying and by adjusting the blend of organics in order to improve the deformation behaviour of the granules under compressive load.

4.4 Silicon nitride

In the case of Si₃N₄, technical problems shall not be in the foreground of our considerations, but the
emphasis will be put on economical and cost aspects of the powder production. The qualities of commercially available Si₃N₄ powders are very good, and the performance of components made from them is satisfactory even under severe mechanical conditions. But a breakthrough of Si₃N₄-components has not yet happened, because the costs are too high [4]. Besides the machining costs for finishing, the powder price plays an important role. Generally, it can be stated that the powder price should not be higher than 30 US$ per kg.

The possible methods of synthesis for Si₃N₄ are well known from literature [5]. The most common processes are reviewed in this paper, mainly considering costs and quality.

The diimide process results in a high-quality powder, but the costs for the raw materials and the process itself are very high, especially if we take into account that the byproduct ammonium chloride is produced in quantities which are 4 times higher than the product silicon nitride.

Gas-phase processes require high costs for raw materials, the process and safety installations.

The direct nitridation of silicon which is used for the largest powder quantities today causes high costs for environmental protection. In order to obtain the required quality of powders, milling and subsequent chemical treatment are necessary.

The carbothermal synthesis, developed by the Alusuisse-Lonza company, offers the chance to overcome the above listed problems. Starting from silica, carbon and nitrogen, a new process technology has been developed which yields high-quality and low-cost powders [6]. In addition, the process is ecologically beneficial. As compared to the diimide process and gas-phase reactions, the raw material costs are 4 times lower, in comparison to direct nitridation, the factor is 2. Fig. 10 shows a photograph of the powder according to the newly developed process and a microstructure which can be achieved with this powder.

In literature [4], it is mentioned that an ideal powder price of 10 US $/kg should be aimed at, but even the carbothermal process on a large industrial scale cannot reach this target.

5. Desired powder properties

As indicated in the examples above, it is possible to overcome or at least to reduce the typical defects in ceramics by optimizing the powder production and preparation processes. From the experimental work with silicon carbide, zirconia, alumina and silicon nitride, the following conclusions regarding powder properties can be drawn: a narrow particle size distribution with $d_{90} < 2d_{50}$ and $d_{50} < 0.5$ to $1.0 \mu m$ guarantees a good sintering activity and
lower sintering temperatures in order to achieve the required density.

A powder free of oversized grains (e.g. > 2μm) avoids excessive grain growth under regular sintering conditions. The absence of hard agglomerates facilitates the step of powder preparation and allows sintering at lower temperatures, thus resulting in a fine grained microstructure with the well-known positive effect on the mechanical properties of the finished component. A good deformation behaviour of powder granules depends on the composition of organic additives and helps to avoid the formation of large pores during the densification step. Intensive mixing/milling of powders and additives is of great importance in order to destroy hard aggregates and to ensure homogeneous distribution of all the additives.

As demonstrated for silicon nitride, the powder costs can be considerably reduced, if factors such as environmental compatibility and raw material costs are considered accordingly.

6. Conclusions

In order to realize the predicted growth rates in structural ceramics, technical and economical improvements for ceramic powders and components are necessary. One possible solution lies in an integration of the two separate steps of powder production and preparation. This will ensure better qualities of the ready-to-use sintering mixes and lower the costs considerably. Different types of feedstock such as spray granules for dry pressing or slip casting and compounds for injection moulding or extrusion, will gain an increasing market share instead of powders without additives. The economic and technical benefits will promote the market growth for structural ceramic components.

References

2) K. Niihara, New design concept of structural ceramics – ceramic nanocomposites, The centennial memorial issue of the ceram soc. of Japan 99 [10], 1991, p. 972-982

Author's short biography

Dr. Albert Kerber

Dr. Albert Kerber works for LONZA-Werke GmbH as head of the product and process development department with a priority in high-performance ceramics. After studying chemical engineering he gained a doctorate in engineering at the Technical University of Karlsruhe with basic studies on single particle crushing. Before joining LONZA in 1986 he spent one year at the University of Utah in Salt Lake City, USA, under a contract of the Department of Energy, studying the energy efficiency of different modes of size reduction.