Challenges in Two-Component Ceramic Injection Moulding

A. Mannschatz, T. Moritz
Fraunhofer- IKTS Dresden
www.ikts.fraunhofer.de

Introduction

The role of advanced ceramics in engineering structures largely depends on the possibility of reliable mass production of complex-shaped components at acceptably low costs. Because of the near-net-shape production and the economic efficiency in large series powder injection moulding (PIM) is the shaping technique of choice for metal/ceramic parts of complex geometry [1]. The process is capable of providing not only shape complexity but also high precision and high performance properties in the sintered parts [2]. Tolerances of 0,3 % or better are generally claimed by PIM producers. The concept of the PIM technique is based on mixing the ceramic powder with a liquid binder system (usually a blend of molten polymers) to create a viscous feedstock, which is granulated, cooled and fed into an injection moulding machine. The moulding mix is reheated to a high viscosity fluid state and is injected under high pressure into a die cavity. The moulded part is removed after the moulding mix has solidified in the die. The organic binder is then removed from the component at temperatures up to 500 °C, generally by some combination of wicking and thermal decomposition, solvent debinding, catalytic debinding or other. Finally, the component is sintered to obtain its final ceramic properties [3]. Examples of components currently being produced commercially include ceramic turbocharger and radial rotors, alumina thread guides, and rare earth magnet pole pieces for hard disk drives.

In the recent years following trends could be observed in ceramic injection moulding:

(1) Development of multifunctional ceramic components with a high degree of complexity by two-component ceramic injection moulding (2C-CIM);
(2) Combination of contradictory material properties in one ceramic part without additional joining steps; production of ceramic/ceramic- and ceramic/metal-compounds without additional joining by 2C-CIM and
(3) Reduction of processing costs, scrap-rate and tolerances such as an increase of accuracy.

First ideas and patents concerning co-injection moulding of two synthetic materials appeared 40 years ago [4]. To the first applications of two-colour injection moulding belong buttons with abrasion-resistant symbols for computer keyboards or telephones [5]. Indeed, applications from the automotive branch show that co-injection moulding is applied to a great variety of automotive components. By this technique not only different colours but also thermal, mechanical, electrical and optical properties of plastics can be combined in one processing step [5]. Since sintering is performed at temperatures where diffusion bonding is possible, a goal in PIM has been to form green assemblies (by joining prior to sintering) and use the sintering step for diffusion bonding [6].

The ability to manufacture and surface engineer a component in a single process has attractive implications, both technically and financially, particularly when large numbers of complex shaped components are to be produced [7]. First research results have shown that ceramic materials can be combined in one part by 2C-CIM [7-9]. Following model systems have been produced: (1) a component with alumina skin and core, possessing a 0,5 µm particle size skin layer surrounding a 1 µm particulate core [7], (2) toughened components with a skin containing 20 vol.-% partially stabilised zirconia surrounding a 100 % alumina core [8], and (3) a ceramic heater consisting of different Al_2O_3/TiN-mixed ceramics [9]. Moreover, the combination of different ceramic materials and ceramics with metals by two-component injection moulding is described in [10]. Cai et al. [11] studied the co-sintering of alumina and zirconia starting from tape-cast green sheets. All studies on 2C-CIM have disclosed that sintering rate control is crucial to the success of this shaping method. Both components must sinter at similar rates and at similar positions in the sintering temperature profile to avoid delaminations. The sintering behaviour can be altered by lowering the powder content of one mix and hence its green density, at the risk of a porous component or by addition of a second non-sintering composite phase [7]. The variety and combination of materials that can be used in the manufacture of metal or ceramic components by powder co-injection moulding is more limited due to the requirement for compatible sintering characteristics [7]. Depending on the size of the contact area of both ceramic materials the feedstock components can be injected simultaneously or sequentially.

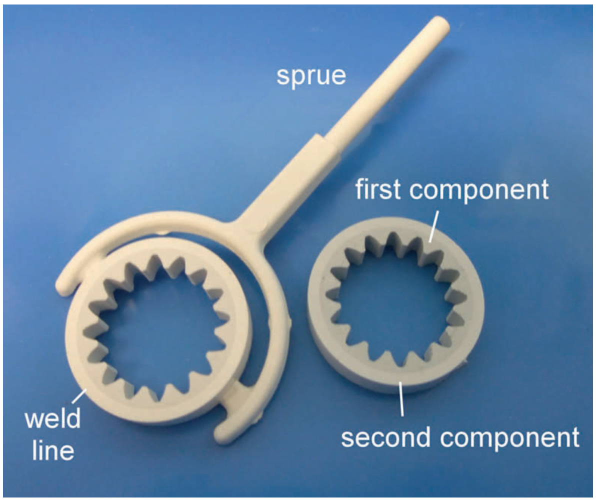
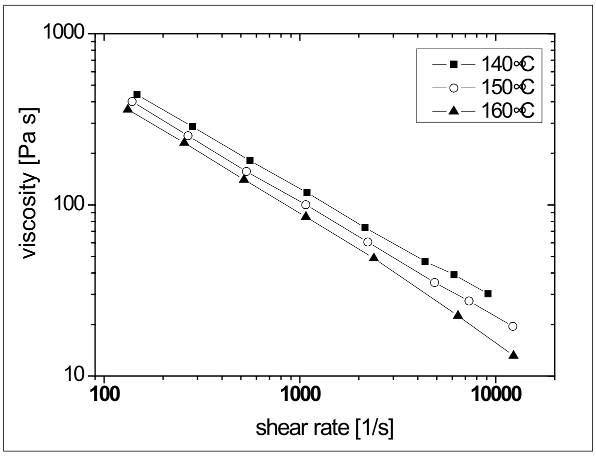


Fig. 1
Gear wheel in green stage with sprue; perpendicular to the gates two weld lines form

Fig. 2
Rheological behaviour of the alumina feedstock at different temperatures



Since September 2006 fourteen partners from industry and RTD from seven European countries have been developing ceramic components for automotive and railway applications by two-component ceramic injec-

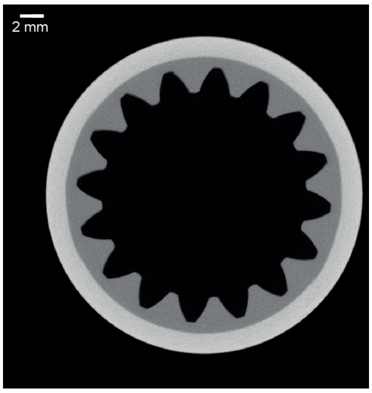


Fig. 3 Computer tomographic image of a green two-component gear wheel

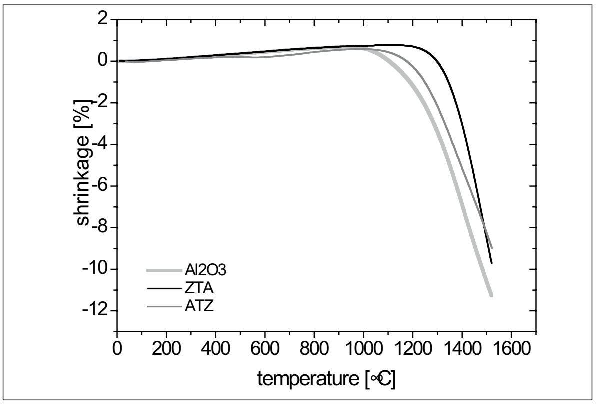


Fig. 4 Sintering curves of alumina, ATZ and ZTA measured on debindered injection moulded samples

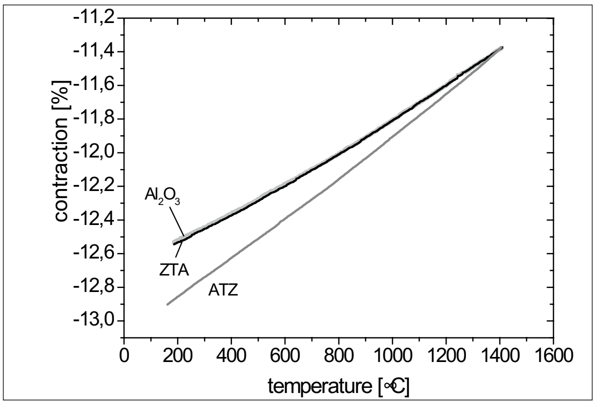


Fig. 5 Thermal contraction during cooling

tion ceramic moulding (2C-CIM) in the frame of the European STREP project "CarCIM". The project will result in four 2C-CIM prototype parts integrated in systems for functional testing and verification such as for techno-economical assessment of the complete processing chain which will be developed in four parallel case studies:

(1) ceramic glow plug,
(2) ceramic gear wheel,
(3) ceramic valve seat, and
(4) ceramic braking pads for high speed trains [12].

This article deals with one of the case study components of the CarCIM project, the gear wheel, for showing exemplarily the requirements which must be met by producers of multi component ceramic parts for avoiding cracks, delaminations or distortion of the products. For that purpose the development of this two-component ceramic part beginning with the choice of the material combination is described. For achieving a prototypical functional ceramic part a gear wheel had been specified by Robert Bosch GmbH which shall consist of an outer though ring and an inner gear ring with high hardness. Two material combinations, alumina toughened zirconia (ATZ)/zirconia toughened alumina (ZTA) and alumina/ZTA, had been taken into consideration and will be compared in this article. A possible application of this specified component could be fluid or fuel pumps.

Experimental

The two material combinations have been realized with three ceramics.

The powder CT3000SG (Almatis) was chosen for the alumina component. It was also used as basic material for the ZTA which was formed by addition of 7 mass% nanostructured zirconia (Evonik Degussa GmbH). The ATZ component consists of PYT05.0-005H (Unitec Ceramics) zirconia powder and 7 mass% fine grained alumina powder (Baikowski) (Tab. 1).

The feedstocks were prepared on a shear roller (BSW 135-1000, Bellaform) using the binder system Licomont® EK583 (Clariant) plus additives for enhanced wetting behaviour. In order to ensure good homogenisation the feedstocks passed the shear roller three times. The raw materials of the particle toughened ceramics were mixed in-situ during feedstock preparation.

For each of the material combinations one feedstock couple was developed having a solids loading of 56,5 vol-% and 55 vol-% for ATZ/ZTA and ZTA/Al_2O_3, respectively. Flowability was tested by high pressure capillary rheometry (RH10, Malvern Instruments).

Two-component injection moulding was performed on a two-component injection moulding machine (320S, Arburg). The two-component part consists of two concentric rings whereas the inner ring holds the gear teeth (fig.1). The tool works with rotary plate technique (tool design: *Fotec GmbH,* tool construction: *Ernst Wittner GmbH*). In a first step the inner component is injected, afterwards the tool opens and turns by 180°. Thereby the first component is transferred into the second cavity and in the second step the outer component is injected. To shorten flow paths the components are filled through two gates. Perpendicular to the gates the feedstock fronts meet and form two weld lines. Within this study three types of gear wheels were produced for which the outer and the inner component will be marked with (o) and (i), respectively: (1) ATZ(o)/ZTA(i),
(2) ZTA(o)/Al_2O_3(i) and
(3) Al_2O_3(o)/ZTA(i).

Green parts were inspected by X-ray computed tomography (CT Compact, Fraunhofer Development Centre X-Ray Technique Fürth and Procon X-ray) to detect injection moulding defects and characterize the interface.

The binder system contains a water soluble component which allows two-stage debinding. Prior to thermal treatment, pores are created by extraction debinding that support the transport of reaction products in the later thermal decomposition. In two-component parts swelling of binder molecules might damage the interface of the green composites. Therefore the samples were only subjected to thermal debinding in air up to 450 °C.

The debindered samples were sintered at 1620 °C for 4 h. Linear shrinkage of the individual feedstocks was determined using one-component injection moulded bar shaped samples (3,5 x 7 x 70 mm³) in order to avoid any interaction with a second component. Sintering behaviour and thermal expansion was studied by dilatometry on debindered injection moulded samples at temperatures up to 1550 °C. Roundness of green and sintered bodies was tested by 3D-coordinate measuring technique.

Tab.1 Powder properties

Powder	D_{50} [µm]	BET [m²/g]
PYT05.0-005H (UnitecCeramics)	1,0	4,3
CT3000SG (Almatis)	0,8	6,5
n-ZrO_2 (Evonik-Degussa)	0,02	43,3
Al_2O_3 (Baikowski)	0,14	19,9

Results and Discussion

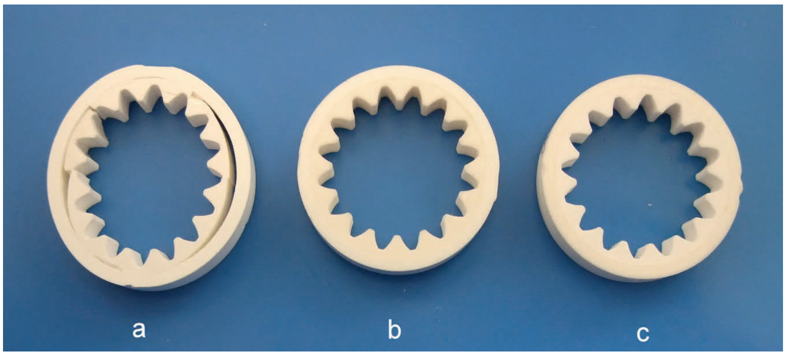


Fig. 6 Sintered gear wheels for the material combinations
a) ATZ(o)/ZTA(i),
b) ZTA(o)/Al$_2$O$_3$(i),
c) Al$_2$O$_3$(o)/ZTA(i)

In 2C-CIM the two materials are joined in green stage and the final composite is formed during co-sintering by diffusion bonding at high temperatures. This means that the partners have to be processed simultaneously and sintering behaviour, thermal expansion as well as final shrinkage have to be considered for material choice.

Final shrinkage is defined by the particle packing density of the green body and the achieved sintering density. In powder injection moulding, the design of the feedstock offers the opportunity to affect the green density by modifying the powder-binder-ratio. In terms of flowability and debinding behaviour the optimal binder content is determined by the powder properties like particle size and surface since the powder particle surface has to be coated completely. While lacking of binder decreases injectability excess binder leads to powder binder separations. Therefore, owing to the differing powder particle sizes for each feedstock couple the binder and additive composition was adapted individually to result in equal solids loadings. High pressure capillary rheometry showed that all developed feedstocks were suited for injection moulding since their viscosities were well below 1000 Pas [13]. Because of the shear thinning behaviour the viscosity decreases with increasing shear rate, and at higher temperatures the viscosity decreases due to improved flowability of the binder components (Fig. 2). The injection moulded green gear wheels were flawless for all feedstock combinations.

Non-destructive testing by X-ray computed tomography showed that no injection moulding defects like bubbles appeared and that the first component was not damaged by injecting the second feedstock (Fig. 3). The interface could be established defect-free without stress-induced cracks. In two-component injection moulding, stresses might arise between the two components if the feedstocks undergo differing thermal contraction while cooling from processing to room temperature or if the temperature difference beween first and second component is too high in the moment of joining. This effect can be limited by using the same binder system.

By adapting the solids loadings shrinkage adjustment was accomplished. According to the higher binder content the shrinkage of ZTA/Al$_2$O$_3$ was higher (ZTA: 16,8 %, Al$_2$O$_3$: 16,3 %) than for ATZ/ZTA (ATZ: 15,7 %, ZTA: 15,4 %).

Besides the final shrinkage sintering kinetics play an important role. Dilatometric measurements reveal that the used materials start to densify at differing temperatures (Fig. 4). By addition of zirconia the sinter temperature of the alumina is shifted towards higher temperatures since the ZrO$_2$ particles hinder grain growth in ZTA. The onset temperature moves from 1150 °C to 1280 °C and the maximum shrinkage difference is 3,9 % in Al$_2$O$_3$/ZTA. For the combination ATZ/ZTA the onset temperatures vary by 80 K and the maximum shrinkage difference of 3.0 % is slightly lower. The shrinkage mismatch can cause stresses between the two materials which is especially critical for the less sinter active component, since it is still in initial sintered or even debindered state and only weak particle interactions contribute to the strength. After sintering the parts cool down to room temperature and shrink according to their coefficient of thermal expansion (CTE). The CTEs of alumina and ZTA were comparable with 9,35*10^{-6} K^{-1} and 9,48*10^{-6} K^{-1}, respectively (Fig. 5). In contrast, ATZ has a CTE of 12,05*10^{-6} K^{-1} and contracts to a higher degree.

Despite of the differing shrinkage intervals defect-free gear wheels with intact interfaces could be obtained for the combination Al$_2$O$_3$/ZTA. However, for ATZ/ZTA the inner ring was destroyed at the weld line (Fig. 6). In parts whose outer components sinter at lower temperatures (ATZ(o)/ZTA(i) and Al$_2$O$_3$(o)/ZTA(i)) the inner ring is subjected to compression stresses. If those stresses exceed the limiting strength the inner component is damaged at critical sites like in ATZ(o)/ZTA(i) at the weld lines. In this case additional forces are applied during cooling because of the greater CTE of the outer ring. In Al$_2$O$_3$(o)/ZTA(i) the comparable CTEs allow synchronal contraction and the samples remain defect-free.

In the couple ZTA(o)/Al$_2$O$_3$(i) the reverse forces act because the inner ring sinters earlier and applies tension forces onto the interface. The SEM image in fig. 7 shows the bottom of a gear tooth and emphasizes how well the interface was established already in green state. While the alumina starts to sinter cracks

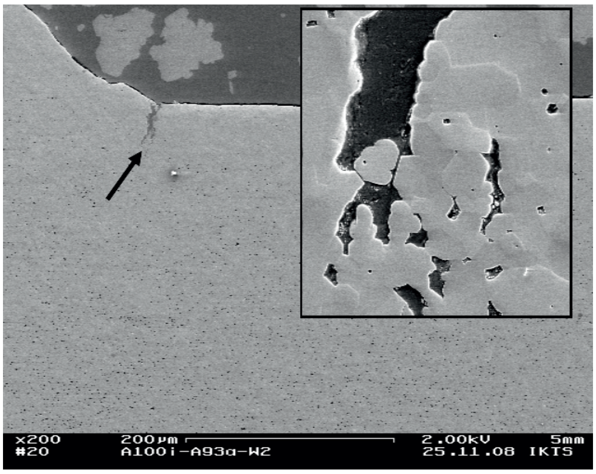


Fig. 7 SEM image of bottom at gear tooth with alumina as inner component

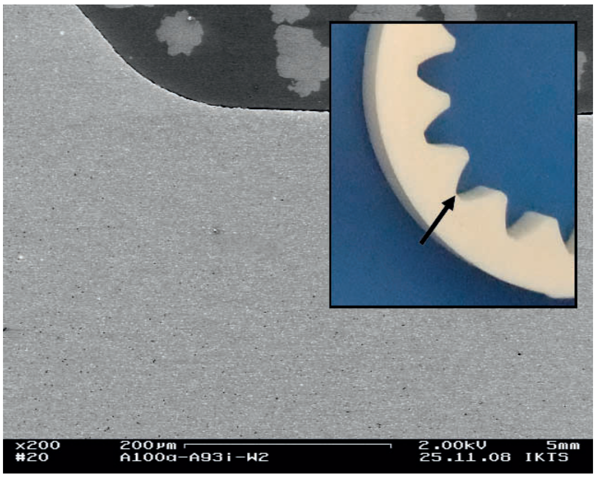


Fig. 8 SEM image of bottom at gear tooth with ZTA as inner component

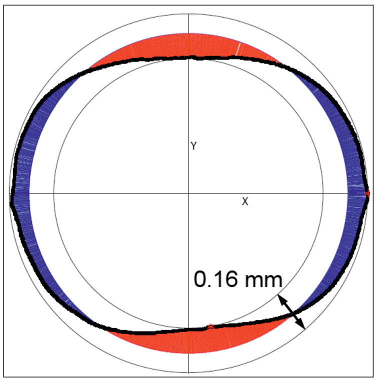


Fig. 9
Outer diameter of sintered sample with a mean diameter of 22,9 mm determined by 3D-coordinate measuring technique; deviations from roundness are displayed enlarged

form instead of delaminations between the two components. For the combination Al_2O_3(o)/ZTA(i) the stress conditions prevent crack growth (Fig. 8).

The diameter of defect-free samples was measured by 3D-coordinate measuring technique around the whole circumference. Only small deviations from roundness were found which are displayed enlarged in Fig. 9. The slightly elliptic shape can be referred to the location of the gates at the part. While the smallest diameter was found at the gates, the largest dimension was at the weld lines. This could already be observed at green samples with the diameter of 27,09 ± 0,02 mm. During sintering this effect is enhanced by possible marginal lower packing densities at the weld lines. For ZTA(o)/Al_2O_3(i) and Al_2O_3(o)/ZTA(i) the diameter was 22,83 ± 0,09 mm and 22,98 ± 0,07 mm, respectively.

Conclusion

Two-component ceramic injection moulding is a very promising shaping technique for large-scale production of ceramic parts with novel functionalities and complex geometries. The advantage of this technology can be seen in the fact that two different ceramics can be combined without any additional time-consuming and expensive assembling or joining steps. However, two-component ceramic injection moulding is a very challenging shaping method. For each processing step of the technological chain both ceramic materials have to be adjusted to each other. Following principle requirements should be taken into account for the development of two-component ceramic parts:

1. The powders chosen for two-component injection moulding must be sinterable to full density at comparable temperatures and under the same gaseous atmosphere.
2. For avoiding critical stresses during sintering the powders shall have a similar sintering behaviour, i.e. the onset of shrinkage shall fall in a narrow temperature range for both powders and the shrinking rate shall be comparable.
3. For ensuring a precise adjustment in total shrinkage the volume content of solid in the feedstocks must be the same.
4. Since differences in the thermal expansion coefficents of the feedstocks may cause cracks, distortion or delamination of the compounds already in the green state the same binder system or binder systems with comparable thermal expansion behaviour must be used for feedstock preparation.
5. The thermal expansion coefficients of the sintered ceramic materials play also a very important role as shown in this article, because differences in this property can result in stresses in the two-component part during cooling after sintering or during application of the part under cyclic heating and cooling conditions.

If stresses between both components cannot be excluded totally, they should be taken into consideration already in the design of the injection moulded parts. For the experiments we carried out with the three ceramic materials the most critical aspect for the two-component parts has been the difference in the thermal expansion coefficient between the materials ZTA and ATZ.

Acknowledgement

The CarCIM project is funded by the European Commission within the 6th Frame Programme (TST5-CT-2006-031462).

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