Aspects of Economical Production of Silicon Nitride Injection Molded Components

Silicon nitride is a promising engineering material characterized by the special combination of its properties such as extremely high strength and toughness, low thermal expansion, good thermal conductivity, high hardness, and extremely high chemical resistance [1, 2, 3] With this property profile, silicon nitride is predestined for extreme mechanical and thermal operating conditions as well as the highest reliability requirements. Despite great efforts in research and development over the past decades, silicon nitride has not yet been able to establish itself in a broad range of applications for cost reasons. Possible concepts for reducing manufacturing costs will be presented in this article.

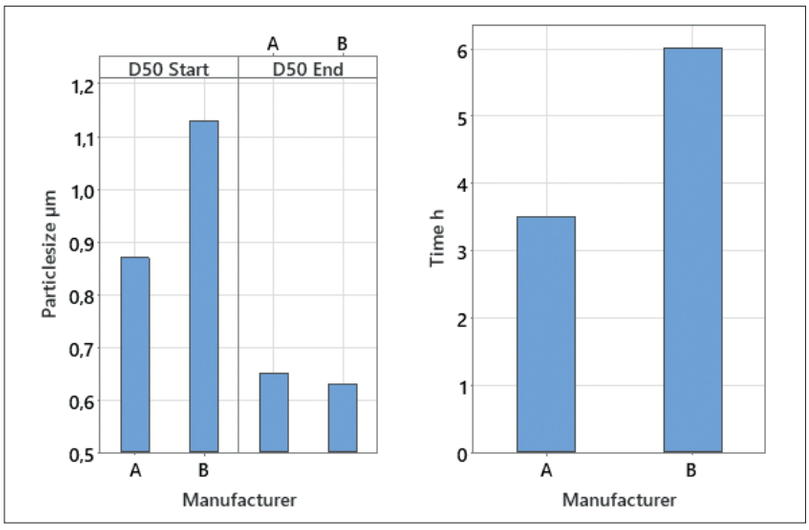

Fig.1
Results of milling the silicon nitride suspensions for spraying

Introduction

The process chain for manufacturing ceramic components is characterized by numerous individual steps, each of which has a considerable influence on the performance of the products and generates specific production costs. The development of an economical production route requires, on the one hand, the identification of possible cost origins and, on the other hand, compromises in the achievable target values [4]. Using the example of a turbine wheel, impulses for more efficient, economical process steps are to be given for complex, large-volume silicon nitride components. These process steps include raw material preparation, shaping by injection molding and heat treatment. Energy and thus costs can be saved here, for example, by shortening the milling time, improving raw material utilization through a near-net-shape molding process and shortening the combined dewaxing and sintering processes.

Powder preparation

Costs can already be specifically influenced during raw material selection and preparation. For the raw material preparation in the form of mixed milling for comminution and mixing with the sinter additives and subse-

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silicon nitride, turbine wheel, CIM, gas pressure sintering

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quent binder-free granulation, ball milling processes with subsequent aqueous spray granulation are used.

Comparatively, two silicon nitride materials from European manufacturers with comparable raw material prices were investigated in more detail. Identical powder preparation processes with the same sintering additives were carried out with both raw material grades. Milling time and ball wear in the milling process were identified as outstanding cost factors. The two starting raw materials differed in initial particle size and were ground down to identical specifications. With comparable target values in the D50 and D90, twice the milling time was required for raw material B compared to A, Fig. 1. In addition to the increased milling time, increased wear was also observed in the milling balls for powder B. The milling time and ball consumption can thus be significantly reduced by the clever selection of a suitable raw material close to the target specification.

For further cost optimization, additional standard preparations were carried out with manufacturer A, but the grinding balls were also varied. In the comparative tests of the powder raw materials, only balls made of high-quality silicon nitride were used. However, significantly cheaper balls are also available on the market in Europe, which are manufactured using a different process. Until now, however, it was not known to what extent this quality could be used in silicon nitride processing. Increased grinding ball abrasion can lead to a reduction in component quality during the sintering process. Under identical grinding conditions, these two ball grades were tested.

This showed that although the wear of the low-cost balls B was slightly higher, in the end significantly lower costs were incurred (Fig. 2). Since the milling time was even somewhat lower than with the cost-intensive ball, it can be assumed that the grinding effect was just as effective. In raw material preparation, optimization in raw material selection and process control can thus result in considerable cost savings by shortening the milling processes and saving energy consumption and operating resources.

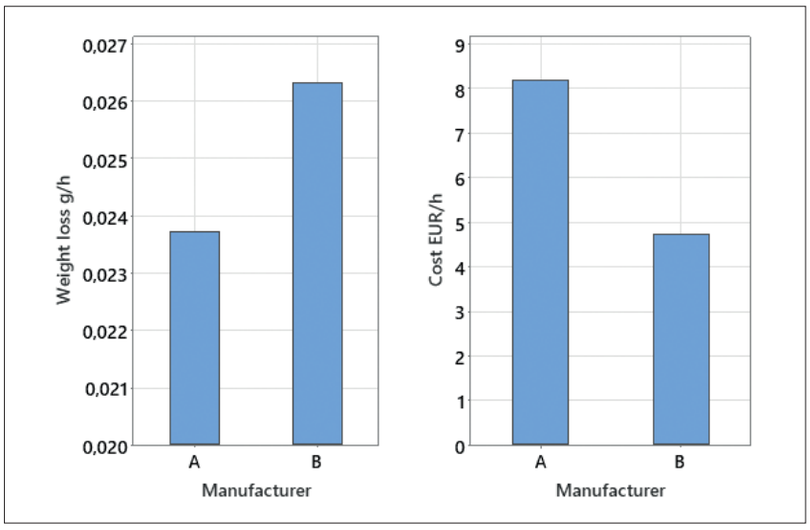


Fig. 2
Comparison of different grinding ball qualities

Development of customized injection molding feedstocks

So-called feedstocks are required to produce components via injection molding. These feedstocks have an organic binder system consisting of engineering thermoplastics, waxes, and wetting additives for the flowability required for molding. One advantage of these wax-containing binder systems is the possibility of multi-stage dewaxing. By means of an isopropanol bath, kerosene, for example, can be dissolved very well at temperatures of approx. 75 °C. This multi-stage debinding allows thick wall thicknesses, such as those found in a turbine wheel, to be converted. Thick wall thicknesses often tend to crack during thermal debinding due to excessive binder decomposition, so that the components must be discarded. Due to the very fine silicon nitride powders, it is challenging to produce both feedstocks with good flowability and good binder extraction. This requires specific adjustment of the binder additives and their proportions.

To achieve a high degree of extraction in solvent, the proportion of these components must be maximized, but this is accompanied by high solidification shrinkage and a reduction in green strength due to high brittleness. Special additives as mold release agents and for adjusting the wetting or compatibilization of the individual organic components are also necessary for reproducible, low-variation processing. In solvent processes, especially with long process times, there is always the risk of swelling of the organics, which can lead to deformation or defects. Two measures can improve binder extraction: First, increasing the binder components that do not swell in the organic solvent used, and second, increasing the soluble components in addition to using a resistant backbone. The first option is particularly effective for thin-walled components, while a high extraction level favors high wall thicknesses. A binder formulation developed for this purpose with approx. 30 mass-% HDPE, 60 mass-% waxes and 10 mass-% process additives proved to be suitable with regard to these requirements. This feedstock formulation is suitable both for production on twin-screw extruders and on a shear roller.

Injection molding of turbine wheels

An existing injection mold for turbine wheels at IKTS was used to demonstrate and test the injection molding materials (Fig. 3). The outer diameter for the injection molded part is approximately 80 mm and wall thicknesses range from 0,7–12 mm. This mold is equipped with eleven openable jaws for 11 turbine blades and offers the possibility to adjust the shaft support according to the requirements of the joint. Injection molding of the turbine wheels was carried out on an Arburg 470S specifically equipped for powder injection molding with a 30 mm screw. The processing temperatures of the polyethylene – wax feedstocks ranged from 130–160 °C, and mold temperatures between 45–60 °C were used. The injection time was 0,8 s with a total cycle time of 49 s. The high total cycle duration is necessary for stable solidification

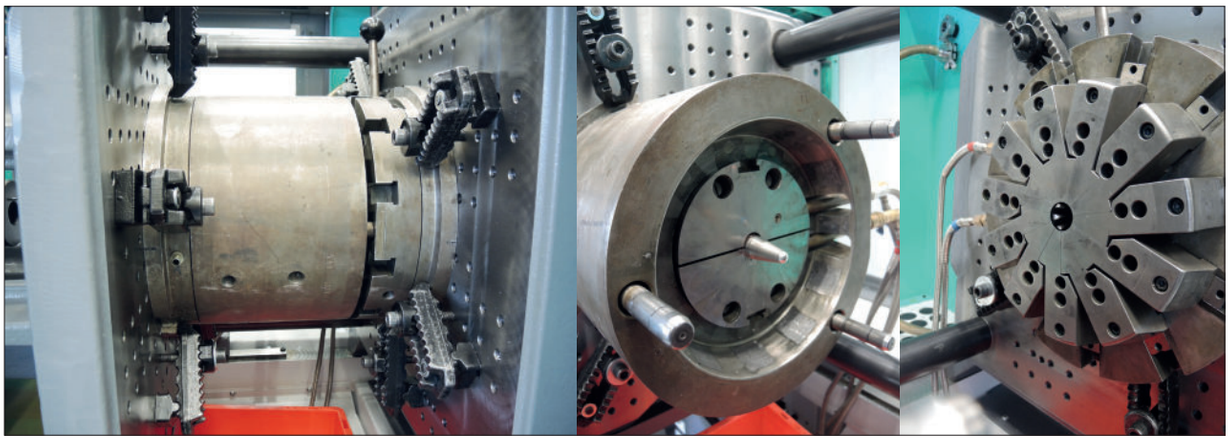


Fig. 3
IKTS turbine wheel injection mold

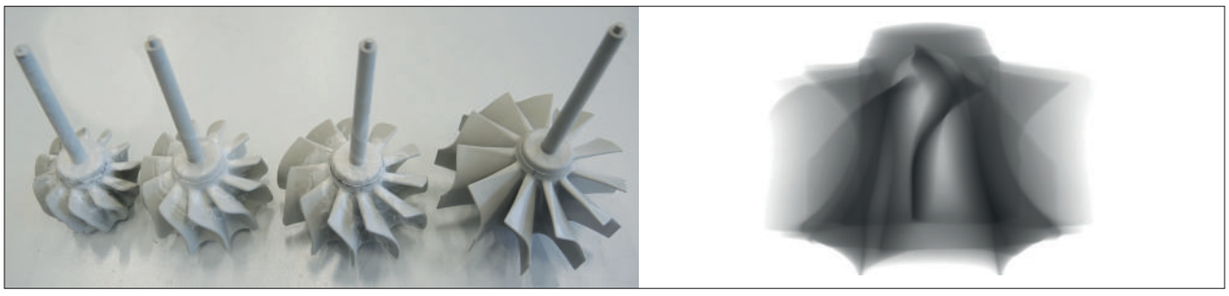


Fig. 4
Mold filling behavior of applied silicon nitride feedstock (left); radiographic picture of green turbine wheel (right)

of the feedstock and subsequent demolding without damage and deformation due to the high residual cooling time.

The mold filling behavior for the developed feedstock formulation is shown as an example in the Fig. 4. A uniform filling of the cavity without Jetting formation can be seen. CT examinations of the green parts did not indicate any defects in the form of air inclusions, contraction vacuoles or stress cracks.

Solvent extraction as first step dewaxing

One of the focal points in the development of the processes is the defect-free dewaxing of the large-volume demonstrator components. In addition to the goal of defect-free processing, processes have also been developed and investigated that reduce the number of individual process steps as far as possible. It is advantageous to carry out the dewaxing of thick-walled injection molded components in two stages: Pre-extraction in an organic solvent is followed by thermal decomposition of the organics. Ideally, the solvent is so successful that the remaining organics can be removed in a so-called combined firing process prior to sintering by a slow heating rate or holding time in the debinding area. Limitations are set here by the component wall thickness or the maximum permissible residual free carbon content. The latter prevent complete compaction in the sintering process and should therefore be avoided as far as possible. For this purpose, thermal debinding under exclusion of air, as carried out in a combined firing process for silicon nitride, can be preceded by an upstream burnout under air.

For binder extraction with organic solvents, various commercial plants are available in different sizes with integrated solvent recir-

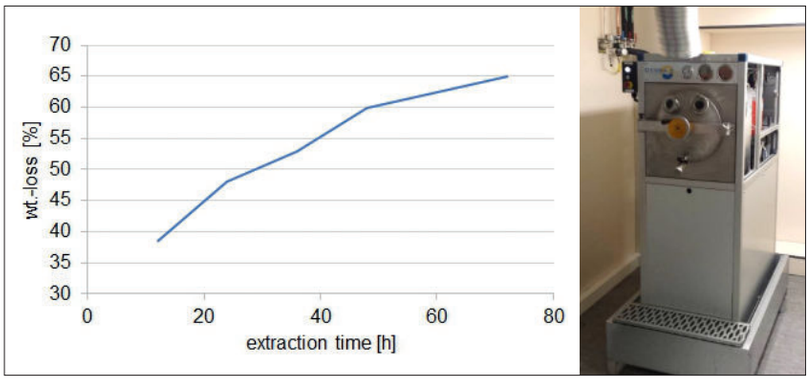


Fig.5
Dewaxing behavior by solvent extraction in isopropanol within 72 h (left); applied solvent extraction device Desbatec MDU30 (right)

culation or purification. A Desbatec MDU30, Sulzbach am Main/DE, was used for these investigations (Fig. 5).

Depending on the wall thickness, the extraction cycles include a total duration between 12–72 h in isopropanol at a process temperature of 75 °C followed by 6–12 h of drying at 40 °C in the extraction chamber. Too short extraction cycle or unsuitable polymer formulation can lead to cracks in thickest areas caused by swelling or drying issues (Fig. 6). Depending on the loading, different component mass/solvent ratios can occur, which must be considered. The saturation of the solvent turned out to be an important influencing factor. An excess of solvent can significantly increase the solution quantities. Due to the high number of components with simultaneously high component mass, this is an important parameter for later efficient series production. For the applied materials a feedstock/solvent ratio of 1 kg feedstock to 30 l solvent show sufficient results. The developed feedstock formulation allows these long extraction cycles, as swelling and drying defects are effectively avoided. In 24 h approx. 50 mass-% respectively in 72 h 65 mass-% of binder were solved (Fig. 5).

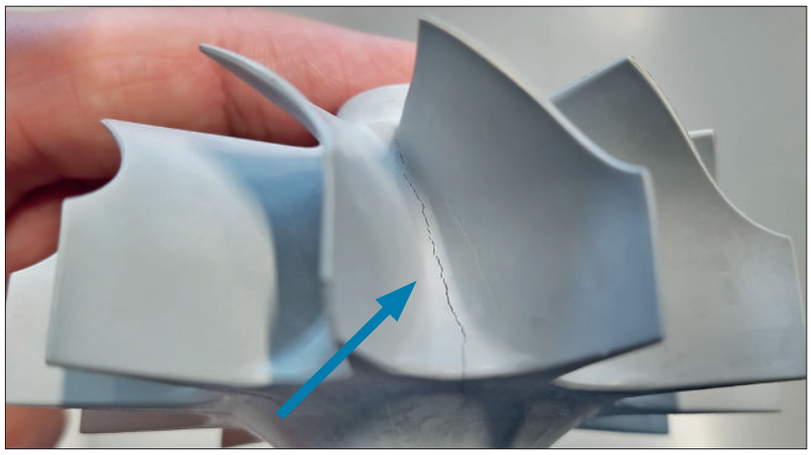


Fig. 6
Typical cracking after solvent extraction process caused by swelling and drying

Thermal Processing

In addition to air debinding processes, more efficient combined firing processes are also established, which in the case of silicon nitride are carried out under nitrogen preferably. Unlike oxidative processes, polymer pyrolysis, i. e. cracking of the polymer chains, occurs under nitrogen. These processes take place under different temperatures than in an oxidative burnout. Extensive thermal analyses of the decomposition behavior were carried out to determine the process parameters, Fig. 7.

Under oxidative atmosphere, the binder formulation used shows a linear mass loss in a temperature range from about 200 °C to 400 °C, with three intense decomposition peaks at 220, 285 and 356 °C, resüectively. These peaks are then usually accommodated by a low heating rate in the temperature regime. Under nitrogen, pyrolysis takes place in a concentrated manner in the range between 400–500 °C. In this range, the temperature in the furnace must be increased correspondingly slowly, so that a large quantity of decomposition products is not suddenly released and the resulting high gas pressure inside the sensitive powder body does not cause any damage, especially in areas of considerable wall thickness.

In a direct comparison of the thermoanalytical results, it is noticeable that the final mass loss is almost comparable under both conditions. Under nitrogen, still a small amount of free carbon from pyrolysis probably remains. Too high a proportion of free carbon can hinder the densification of the sintered components, since the glass phase can no longer wet the powder particles without interference [1, 5]. A high excess of carbon must therefore be avoided at all costs.

However, the sintering tests showed that the density of the parts treated purely under nitrogen was lower than that of the components dewaxed in air. For this reason, upstream air debinding up to 380 °C is recommended for particularly thick-walled components, in which a large proportion of the organics is already oxidized. In contrast, combined dewaxing and sintering processes are possible for conventional wall thicknesses for ceramic injection molding of up to 6 mm.

Based on the turbine wheel geometry, it was further demonstrated that large wall thickness differences can be realized in a combined debinding of extraction and ther-

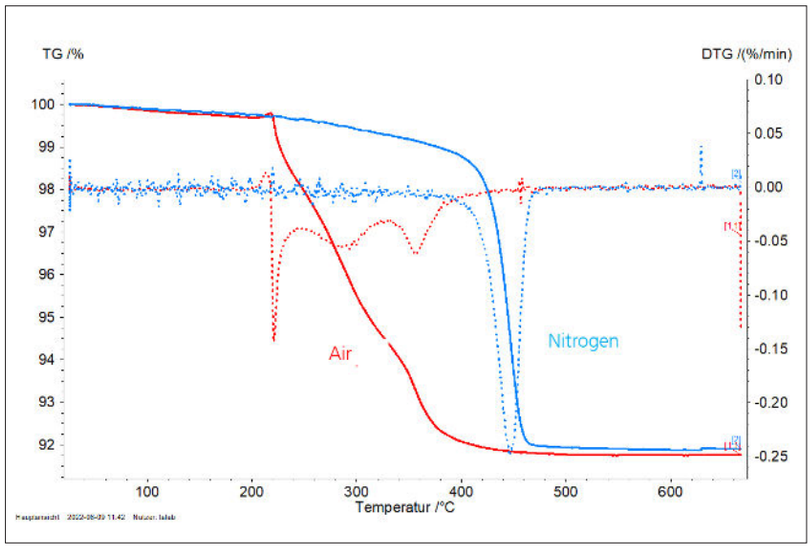


Fig. 7
TG/DTG-analysis: decomposition behavior of applied feedstocks

Fig. 8
Gas pressure sintering furnace (type FP W 90, FCT Systeme GmbH)

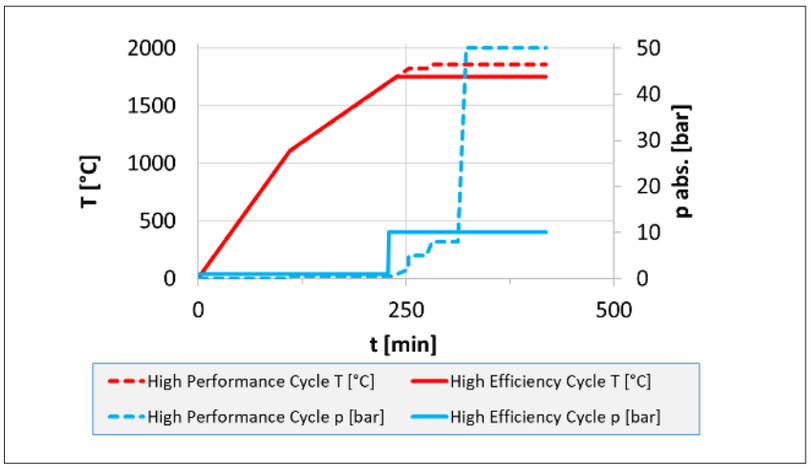


Fig. 9
Applied combined dewaxing and sintering cycle

mal decomposition with adapted organics and process parameters. This allows the realization of very complex, near-net-shape and large-volume components.

Sintering of the turbine wheels after the different debinding steps was done in a Gas Pressure Sintering (GPS) furnace (type FP W 90, FCT Systeme GmbH, Fig. 8). The special feature of the GPS process is a three-step sequence of (1.) debinding at low gas pressure and temperature, followed by (2.) sintering at normal gas pressure/moderate temperature and, after a status is reached with only closed pores being present in the material, finally (3.) sintering at high gas pressure/temperature, which results in a further densification and faster elimination of the remaining pores. If the sintering parts are containing materials, which tend to decompose and/or evaporate at sintering temperature – e.g., silicon nitride used for the turbine wheels – the elevated gas pressure can suppress these harmful processes to a large extent.

Therefore, materials consolidated by GPS show in general mechanical properties (hardness, strength, Weibull-modulus, fracture toughness) which are superior to those of materials produced by conventional sintering method [1].

The parameters for sintering were determined based on various requirements (Fig. 9). Competing aspects here are the required performance of the components and the economic framework conditions of the heat treatment. Ideally, depending on the sintering additive system used, the silicon nitride materials are sintered at over 1800 °C to enable very good densification and at a very high superimposed gas pressure of, for example, 50 bar nitrogen (High Performance Cycle) [1, 5]. However, regulatory requirements make it worthwhile to run the processes below 20 bar and at the lowest possible temperatures to save energy (High Efficiency Cycle). Moreover, lower process pressures and temperatures allow larger or more economical furnaces for series production.

The runs investigated differ in terms of debinding (air pretreatment of individual components), target temperature, pressurization, and residence time in the sintering area. For combined debinding and sintering, a reduced heating rate of 1 K/min was specified in the range between 300–550 °C to allow gentle decomposition of the remaining organic components.

The crucible material shows a considerable influence on the sintering results. Therefore, graphite-free crucibles were produced by slip casting from the material NSN (nitride-bonded silicon nitride, Fig. 10).

In this way, reactions with graphite, which is the usual material for crucibles, were to be prevented as far as possible. The sinter density achieved here varies between

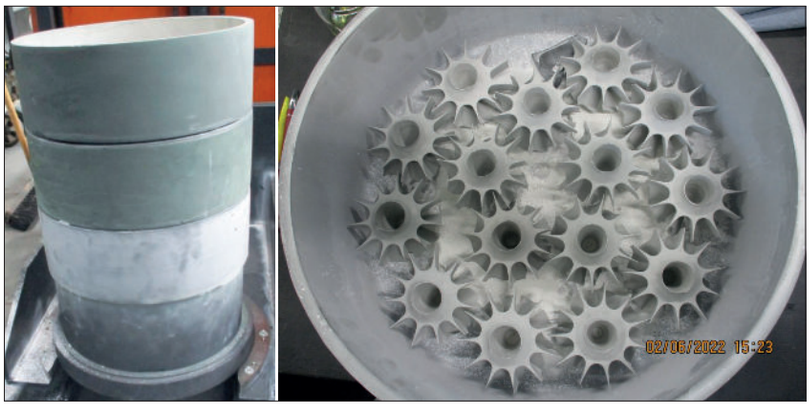


Fig. 10
NSN sintering crucibles for GPS of silicon nitride turbine wheels: crucible stack (left); view into a crucible (right)

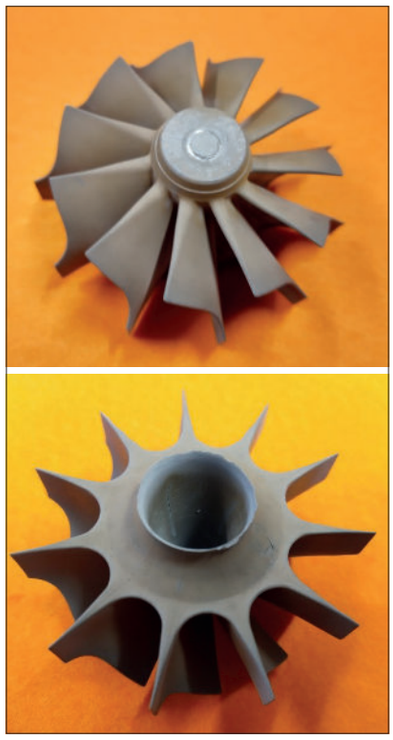


Fig.11
Sintered silicon nitride turbine wheels

3,22–3,25 g/cm³ (Tab. 1). Depending on the application, these values meet the required specifications [1, 4].

Roughness of as sintered surfaces

Surface roughness was determined tactilely on the surface of the turbine wheels and are directly attributable to the firing conditions that existed on the component. A temperature reduction of 100 °C has a positive effect on the surface finish despite low process pressures. The Ra value determined is approx. 1 µm at the lower sintering temperature, and 2,16 µm for 1860 °C (Tab. 2). Laser scanning investigation prove these tactile measurements. Depending on the application, complex grinding finishing of the sintered surface can be dispensed with.

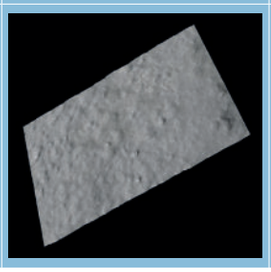
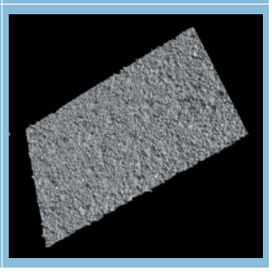
Microstructural investigations

For a more detailed assessment, the sintered microstructure was investigated at the scanning electron microscope. For this purpose, samples were separated from the thickest-walled areas of sintered turbines, embedded and polished (Fig. 12). In terms of grain size, grain boundaries, pores or glass phase distribution, no difference

Tab.1
Sintered density

Cycle	Dewaxing Atmosphere	Sintering Temperature [°C]	Max. Pressure [bar]	Holding Time [h]	Sintered Density [g/cm³]
High performance	Air up to 380 °C	1860	50	2,2	3,25
High performance	Nitrogen	1860	50	2,2	3,22
High efficiency	Air up to 380 °C	1750	10	3	3,24
High efficiency	Nitrogen	1750	10	3	3,21

Tab. 2
Surface roughness properties

Sintering temperature	1750 °C	1860 °C
Fired density [g/cm³]	3,24	3,25
Ra value [µm]	0,995	2,16
Laser scanning investigation		

can be detected in the bulk between the two sintering temperatures. Sintering at 1750 °C already show very good compaction comparable to the reference at 100 K higher sintering temperature. Measured differences in sintered density are not visible for investigated samples.

At higher sintering temperatures, a loss of silicon is observed on the component surface, which produces a fissured surface (Fig. 13). This effect is responsible for the much higher Ra values of the surfaces, which may require mechanical finishing. A final evaluation of the different sintering temperatures is, however, only possible after mechanical characterization and testing. Differences between the different cycles are to be expected, particularly in the Weibull modulus and the associated reliability [6].

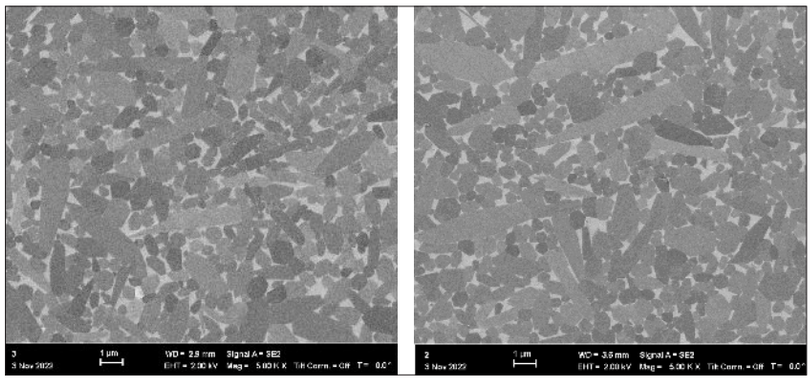


Fig. 12
Scanning electron microscope investigation of bulk: 1750 °C, 10 bar (left); 1860 °C, 50 bar r(ight)

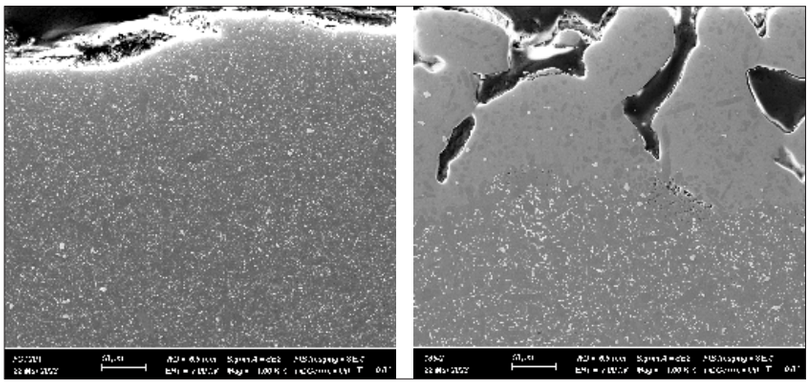


Fig. 13
Scanning electron microscope investigation of surface cross section: 1750 °C, 10 bar (left); 1860 °C, 50 bar (right)

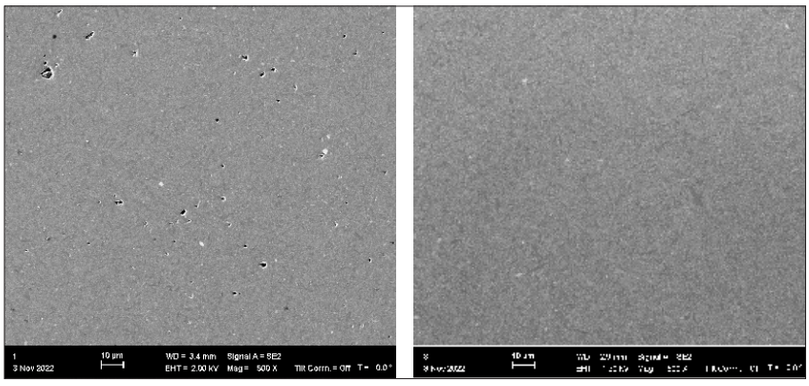


Fig.14
Scanning electron microscope investigation: 1750°C, 10 bar both; N_2 dewaxing in combined process (left); air debinding (right)

A comparison of the combined firing with upstream air debinding still shows significant carbon inclusions, which prevent complete densification(Fig. 14). This means that a air dewaxing is still necessary for thick-walled components. For smaller components with lower wall thickness, however, a combined firing is an economical alternative.

Conclusion

Until now, the high cost of manufacturing silicon nitride components has been one of the obstacles preventing wider use of the material. As a representative example, the turbine wheel demonstrates an economical production of large-format silicon nitride components. It is now possible to significantly reduce production costs through more cost-effective raw material preparation, material-saving and efficient shaping by injection molding, and energy savings in heat treatment. Due to favorable production costs, new fields of application can be addressed that were previously inaccessible due to the cost structure. Areas of application can include components in the textile industry, such as thread guides, but also tribological components, such as sealing discs, rolling bearing components or even valves in the cylinder heads of combustion engines for Liquefied Petroleum Gas (LPG), e-fuels or hydrogen.

Acknowledgement

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