Silicon nitride based ceramics for foundry application

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0. Introduction

Due to its very specific set of material properties, silicon nitride based ceramics have gained a lot of interest in the past 20 years. Many new approaches in technical equipment like gas turbine engines, motor engines, cooking systems, bearings, cutting tools, substrates and ... and many more were investigated with corresponding national and international research activities. However, except of bearings and cutting tools, none of these expected high volume application yet went into industrial production. On the other side, many less spectacular applications are state of the art today and have opened a wide field for niche products and led to new technical solutions with higher service time, less wear and corrosion and improved process and product properties.

Different materials are described in literature and company brochures like gas pressure sintered silicon nitride (GPSN), SiAlON, Syalon, reaction bonded silicon nitride, nitride bonded silicon carbide and so on. Mainly GPSN and SiAlON are named as grades to be used in foundry application. Like in metallurgy, there is no longer only one grade of GPSN or SiALON but a rather wider variety with different properties and compositions.

In this paper, the properties of GPSN grades as well as the production procedure are described shortly. A wide range of application examples are given, to show the state of the art in technical application of silicon nitride and its further potential.

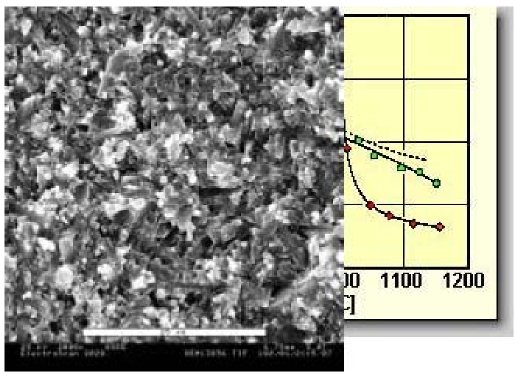
1. Material and properties

1.1. Material

Different grades of silicon nitride based ceramics are offered on the market. I will only concentrate on dense sintered material, because this has to be used if high strength, fracture toughness, thermal shock and high wear and corrosion resistance is required.

Gas pressure sintered silicon nitride (GPSN) is a silicon nitride with different amounts of different oxides as sinter additives. Most common composition contains 5-10 wt% of a mixture of Alumina, Yttria, Magnesia, Spinel, Silica and rare earth oxides. During sintering a SiAlON-phase may be partially formed but must not necessarily. GPSN can be produced more reproducibly, and typically this grades of material show much better fracture toughness and strength as the most important properties for use in foundries. Therefore most mayor suppliers meanwhile offer GPSN for foundry applications, because there is no benefit in using SiAlON. SiAlON only performes better in wear applications where a higher hardness is required.

SiAlON is a ceramic material with a very specific composition range and specific crystallographic structure. SiAlON grains are bonded with a glassy or partial crystalline phase of oxides like Al_2O_3, MgO, Y_2O_3 and other RE-oxides. It is also used as a trade name from some companies, although they not only sell SiAlON but also gas pressure sintered silicon nitride grades.



<u>picture 1</u> rough cracked surface <u>picture2</u> wetting behaviour of ceramics indicating the high fracture toughness

Another issue is the wetability. There, it can be stated that pure aluminium is not wetting silicon nitride but as there is no pure aluminium in technical use, silicon nitride components are wetted more or less depending on the specific chemical composition and the temperature of the melt. Also corrosion takes place but corrosion rates are also related to chemical composition of the melt, the temperature and the composition of the silicon nitride. Mainly oxides of alkaline and alkaline earth metals as well as copper oxide show potential for corrosion.

1.2. Properties

Properties of silicon nitride based materials and other ceramics are shown in the following table.

Material		**HPSN**		**GPSN**	**GPSN TiN**	**HPSN BN**	**NSiC**	**BN**	**AlN**	**TiN**	**LPSiC**	**SSiC**	**Al_2O_3TiC TiN**	**Al_2O_3**	**Al_2TiO_5**	**SiO_2**	**ZrO_2**
Densification		HP	HP	GPS	GPS	HP	RS	HP	S	HP	S/GPS	S	HP	S	S/RS	S/RS	S
Micro structure Density Porosity	[g/cm3] [%]	3,20 0	3,25 0	3,26 1	3,45 1	2,4-3,0 2-12	2,80 12	2,1 2	3,24 1	5,4 4 2	3,25 1	3,15 1	4,25 0	3,9 5 1	3,15 15	2,30 20	6,0 5 0
Mechan.Prop.																	
Compressive	[MPa]	2.60 0	3.00 0	3.00 0	3.00 0	1.00 0	600	250	1.00 0	500 *	3.00 0	2.50 0	4.80 0	3.0 00	200	200	2.1 00
Bending s RT 1)	[MPa]	700	850	750	850	500	180	80	300	260	510	400	620	350	40	20	850
1200 °C	[MPa]	450	500	450	400		150		250		500	400	600	320			350
Weibull modul m		18	20	20	20	20	20	15	15	15	15	15	18	6	20	15	18
Fract. toughn. K_{IC}	[MPam1/2]	7	8	8	8	9	4	3	3	2	5	3,5	5	4	4	4	10
Youngs modul E	[GPa]	314	320	320	350	250	220	70	350	390	410	400	400	380	20	40	200
Poisson no. ?		0,29	0,28	0,28	0,20	0,25	0,2 0	0,20	0,20	0,2 0	0,19	0,15	0,25	0,2 0	0,28	0,2 5	0,2 0
Hardn. (Vicker)	[GPa]	16	16	16	18	8-15	10	<10	10	20	20	26	19	21	<10	<10	14
Thermal Prop. max. appl. temp.																	
-inert gas	[°C]	1.20 0	1.20 0	1.20 0	1.20 0	1.40 0	1.8 00	1.90 0	1.20 0	1.8 00	1.60 0	1.90 0	1.60 0	1.8 00	1.000	1.0 00	1.2 00
- air	[°C]	1.20 0	1.20 0	1.20 0	1.00 0	1.00 0	1.4 00	700	1.00 0	700	1.50 0	1.65 0	1.00 0	1.8 00	1.000	1.0 00	1.2 00
T melt / decomp.	[°C]	1.90 0	1.90 0	1.90 0	1.90 0	1.90 0	1.9 00	3.00 0	2.20 0	###	2.50 0	3.00 0	2.00 0	2.1 00	1.500	1.5 00	1.8 00
Th. Cond. ? RT	[W/mK]	30	30	30	30	50	20	90	150	30	90	100	20	30	1	3	2
CTE	[10-6K]	3,2	3,2	3,2	6,0	3,0	5,0	2,2	5,3	8,5	4,9	4	8,0	8,0	1,0	0,6	10, 5
Th.shockpar. R_1	[K]	495	598	527	324	500	110	416	129	63	206	213	145	92	1.440	625	324
Th. shockpar. R_2	[W/m]	14.8 39	17.9 30	15.8 20	9.71 4	25.0 00	2.5 30	37.4 03	19.4 07	1.8 82	18.5 06	21.2 50	2.90 6	2.7 63	1.440	1.8 75	648
Electrical Prop.																	

2. Production of components

FCT Ingenieurkeramik GmbH has established a material grade and two processing routes for the commercial fabrication of a broad range of components with different sizes shapes and tolerances.

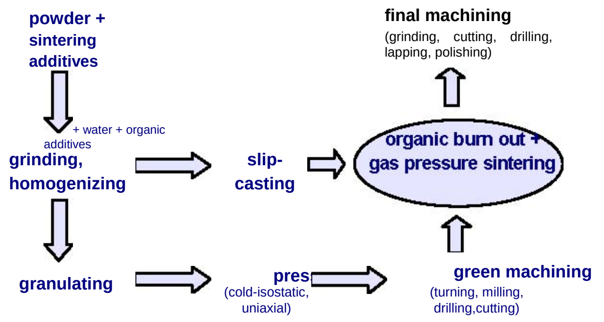
Our standard grade has a composition of 90 wt% Si_3N_4, 6 wt% Al_2O_3, 4 wt% Y_2O_3 which is sintered at 1 MPa of N_2 – gas pressure. Thousands of parts have been produced in the last 5 years for very differen applications and have mostly fulfilled the expectations of our custromers.

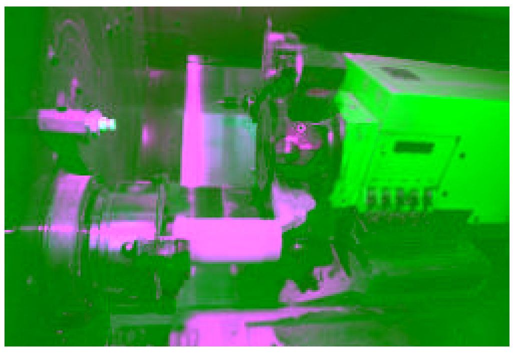
Two fabrication routines are available as shown in the following picture:

1. slip casting for complex, thin walled components

2. cold isostatically pressed preforms with subsequent green machining, sintering and if necessary

final machining by grinding honing, drilling and polishing is done for both.





Picture 3 Production sketch picture 4 CNC turning and milling

Rather large components with length up to 1,25 m but also tiny things with only some mm feed into our product range. We produce prototypes according to customers drawing and also small and intermediate series up to 1.000 pieces per year or fabrication lot. According to wall thickness, complexity and number of parts required we chose slip casting or pressing with subsequent green machining as the shaping technique. So we are in a position to produce any desired design. Typically we give hand to our customers in choosing a “ceramic correct” design or design details.

3. Applications in Light metal and non ferrous foundry industry

One main application area has been located and developed in light metal casting.

Here mainly two materials properties of silicon nitride are required there:

1. excellent corrosion resistance against metal melt
2. excellent thermal shock resistance

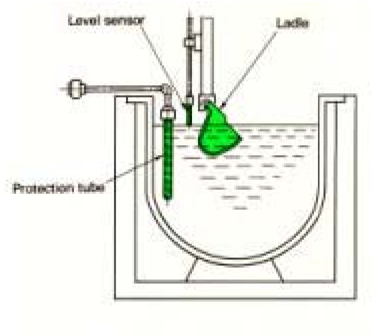
in addition with high strength and fracture toughness which assure a save handling in the tough foundry environment.

Components like thermocouple sheaths, heater sheaths, riser tubes, valve seats and plungers, degassing agitators and a lot of other very specific parts are in use or are tested in new advanced casting systems.

Silicon nitride components are useful for the whole production process of Aluminium parts.

3.1. Melting

Silicon nitride crucibles of can be used for initial melting of metal. Thermal shock, corrosion resistance and high strength guarantee a long service time. Thin walled laddles for taking probes for the inspection of chemical composition as well as for melt dosing are made by slip casting.



Picture 5 melt crucible holding crucible furnace with laddle laddles for melt probing

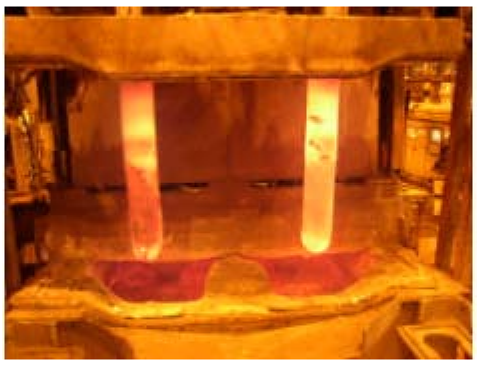
3.2. Melt processing

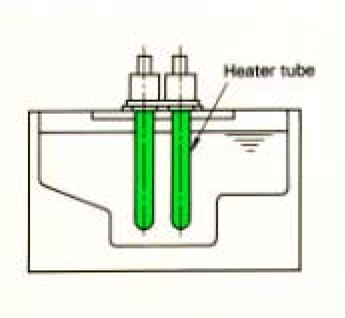
3.2.1 Thermocouple protection sheaths

Thermocouple protection sheaths are meanwhile state of the art in temperature measuring systems for aluminium melt. They are produced in three different standards and length up to 1,5 m. Also larger length were realized by conneting two individual tubes by a high temperature motrar.

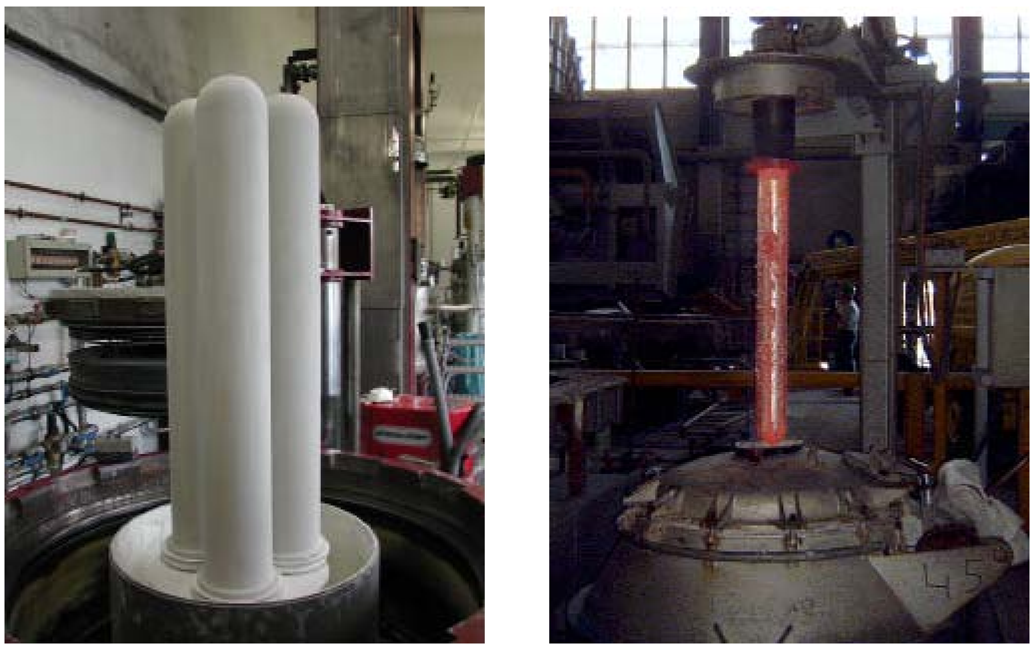
3.2.2 Immersion heater

Melt must be processed, in order to have the desired properties for casting. Therefore it must be kept on the right temperature. This can be done by electrically heated or gas fired immersion heaters. Immersion heater sheaths made of gas pressure sintered silicon nitride show service times up to years. The service time is however dependent on proper handling. Immersion heater tubes are used in filter boxes, casting crucibles and as a new approach in liquid aluminium transport containers. In this new application a new usage of liquid metal will be possible also for small foundries. They can keep the melt liquid over several days and can reorganize their production by no longer preparing their own alloy in small portions.





picture 6 immersion heater green bodies, for a holding furnace, for heating a filter box



picture 7 green bodies in sintering furnace, immersion heater for liquid aluminium transport tank

3.2.3 Degassing agitators

In order to clean the melt, degassing agitators are widely used. They are mainly made of graphite material causing the problem of low service time. Due to the fact, that air and with this oxygen can access to the rotor and more likely to the shaft, the material burns away, and initially the shaft breaks and more often as a following failure the impeller is destroyed too. Using GPSN as shaft in an initial step, the service time can be extended from days to months or even years. Using GPSN for rotors is difficult, because only simple geometries are recommended and the costs are very high compared to graphite. But doing GPSN rotors with an adequate design and proper processing, also service times of months or years are possible.

picture 8 degassing agitator Impeller large shaft and small lab impeller

3.2.4 pumping and dosing

In order to transfer melt from one container to another or into a mould, beside gravity casting and leading the melt through casting lounders, pumping and dosing operations are required where no contamination, also not with oxygen takes place and where a very accurate dosing is possible. This can be realized with a new system, based on a piston pump, where all parts which get in contact with melt are made of silicon nitride. Such pumps are in test and production at some specific customers where the production feasability is tested. With different size of cylinder and piston, different amounts of liquid aluminium, ranging from 0.6 up to 30 kg can be pumped and dosed with one stroke. Using a twin cylinder equipment, a continuous melt flow can be achieved –and any volume can be dosed with a corresponding number of strokes. Additionally a pressure up to 10 bars can reached in the melt. The pump is totally immersed into the melt, only piston rod, valve rod and fixation rods get outside and connect the pump and dosing elements with the corresponding drive and control equipment.

picture 9 pumping equipment for liquid metal pumping and metering

3.3. Low pressure casting

3.3.1 Riser stalks

For low pressure casting of cylinder heads and wheels a special technology has become state of the art within the last couple years. A melt pot with a removable top which can be pressurized up to 10 bar is typically used. The top has one or two riser stalks who feed the molten metal without contaminations via a transfer tube into the mould. The melt therefore is going up and down within the stalk and so introducing a temperature change which causes cyclic stress. Also corrosion takes place because of the additives which are used for the conditioning of the melt. Depending on size, flange geometry, casting conditions and melt composition, service times from 6 month to 2 years are state of the art. These service times lead to dramatically decreased costs for tubes and handling. A factor of 2 can be considered as a typical value. Another benefit is the fact, that the downtime for equipment can be reduced from a weekly cycle, which is necessary for cast iron tubes to a six month or even longer cycle for silicon nitride. Additionally nearly no BN coating is required.

picture 10 low pressure casting equipme
picture 10 low pressure casting equipment for wheels riser tubes of different size and shape

3.3.2. Casting nozzles and plungers In many processes there is a need of dosing

liquid metal during the casting operation.

Seats, plungers and stoppers with finely polished sealing areas are already widely used with very long service times. Up to 1.000.000 cycles are meanwhile reported for the large casting nozzles shown in picture 11.

Picture 11 casting nozzles, seats and stoppers

3.3.3. Wear resistant die inserts and core parts

Some initial experiments were performed with die inserts and cores. The problem which occures is that the metal shrinks on the core if this is not early enough redrawn. As an additional problem, the core broke due to a too narrow fixation in the core holder. The thermal expansion of the core holder metal introduced tensile stress into the ceramic, leading to cracking in a first experiment. But with proper design, there is a good chance to overcome this problems.

3.3 Pressure casting and thixo forging

For semi solid shaping of aluminium, moulds and injection chambers have to be very wear resistant and have to carry a high thermo mechanical load in service. Initial investigations are underway and look promising. A set of shot sleeve and a corresponding piston was produced as a prototype and will be tested in the near future. From other work, we have gained experience with tooling parts for a thixo forging mould which look promising. Also very thermal shock resistant containers for inductive heating of steel rods to their thixo temperature have performed very nice. These results may be transfered to aluminium processing in order to prevent severe mould wear, mainly with casting highly silicon and other particle containing alloys.

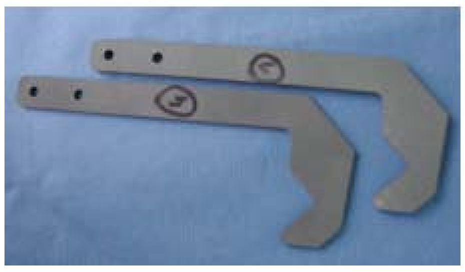
3.4 Rolling

In metal industry, new shaping approaches for even complex part are rolling operations. For such shaping processes steel, WC and ceramic rollers are used. Silicon nitride due to its excellent thermal shock behaviour, high strength, hardness and toughness shows improved service time and product quality even at rolling temperatures up to 1000°C in rolling of stainless steel. Further advantages are the possibility of cooling reduction and the lack of material transfer to the rolled metal. Also by rolling of Aluminium, the tendency of friction welding and material adhesion is significantly reduced. This trend can even be more reduced by using composite material with high content of TiN. But not only for the rolling operation silicon nitride tools are used. Even more benefits will be given by the replacement of steel wear parts like guiding rollers or plates.

picture 12 tools for foil rolling for aluminium, stretch rolling of wheels, guiding rolls

3.5. <u>specialities</u>

For dip aluminizing of piston seal rings special hooks were tested which have to withstand a very strong temperature shock with any immersing and retreat step within several seconds. The hook is mounted on a robot.




Picture 13 aluminizing hooks gas introducing tubes

Another approach can be made with composites, based on silicon nitride having a rather high electrical conductivity. Wear resistant level Sensors can be fabricated. Also complex shaped die inserts can be shaped by EDM-operations.

4. Improved properties

As mentioned above, silicon nitride shows improved application benefits compared to other ceramics or metallic solutions. Mainly in foundry industry, solid silicon nitride components give a much longer service time compared to solutions with coatings. Even more improved properties can be reached by silicon nitride based composite materials. Here, a wide variety of different additives help, to tailor materials for specific use in new advanced technologies. With the addition of TiN for example, the hardness and the electrical conductivity can be adjusted to a wide range of technical requirements. Oxides and non oxides can help to change and improve the corrosion resistance by reduction of wetability for metal melts and metallurgical additives. Composites of silicon nitride and boron nitride can reduce corrosion and the tendency for melt and additives to adhere at the component. Also the thermal conductivity can be influenced by special rare earth oxides. A wide range of possible compositions is still under investigation.

5. Conclusion / Outlook

In the paper it is shown, that a wide range of applications of silicon nitride ceramics have been achieved due to the availability of components with different sizes, shapes and complexity. Small and very precise as well as rather large and complex components can be reproducibly and economically produced with a high standard of quality. Materials and components are highly reliable, also in very tough applications. New technical solutions are though possible for advanced equipment and processing routines. It has however be stated, that the introduction of this high tech material has to overcome many problems. Foundry personel has to be educated in proper usage of such components. The specific properties have to be considered if a new application is intended. The experts of DRACHE and FCT Ingenieurkeramik will give hand and support you as our customer with technical background experience, and last but not least with any desired design of silicon nitride parts.