Product and System Innovation Based on Integrative Design with Ceramic (IDC): Material Alternatives

In the second chapter of the series on ICD the main advanced ceramic materials such as zirconia, alumina, silicon nitride and silicon carbide are presented. Their properties, in particular mechanical properties strongly depend on manufacturing, but also on size and geometry and raw material quality. Therefore data found in literature as well as in suppliers brochures can be used for orientation only.

1 Introduction

Ceramic materials have found their place in designing structural components from mechanical engineering to medical applications. Excluding electrical and other functional properties used for electronic applications advanced ceramic materials are characterized as extremely hard, wear and corrosion resistant and shape stable for long times up to temperatures above 1300 °C. In addition ceramic materials are light with densities from 2,5 to 6,0 g/cm³ and can help to reduce weight and to save energy. Material scientists have learned to improve properties und to develop adapted materials. But still designers have a gap in understanding how to use these materials successfully in new applications. As described in the last issue [1] engineers have to find the proper combination of materials and their production, joining techniques and quality assurance. In addition engineers have to consider the – compared to ductile metals – generally different design with ceramics based on a probabilistic strength calculation because of the different properties and failure mechanisms. For safety cases this means that the requested probability of survival replaces the safety factor and has to be de-

termined by numerical simulations and experiments.

A wide variety of advanced ceramic materials with adapted properties are available such as zirconia, alumina, silicon nitride and silicon carbide, which can be used for a large number of applications. A problem for the potential user is that no tables exist which can be used in an easy manner for design of components. When designing with metals, engineers can use e.g. the "Key to steel – Stahlschlüssel" (*Stahlschlüssel Wegst GmbH*) with 70 000 standards and steel-brands from about 300 steelworks and suppliers. A comparable compendium for ceramics will never exist because the properties, in particular mechanical properties strongly depend on manufacturing, but also on size and geometry as described previously [1]. Data found in literature as well as in suppliers brochures can be used for orientation only. In this issue of our series some properties of selected ceramic materials are listed and described to give a first orientation for starting the integrative design process.

Following the rules of Integrative Design with Ceramics the requirements on material properties should be selected as "necessary" or "eligible". Highest quality is often needed only at the right place but not in the complete component. As an example knifes or cutting tools can be mentioned which are loaded only in small areas. Milling cutters are not manufac-

tured completely of ceramic but ceramic cutting tools are joined to a metal blade where hardness is needed.

Weak properties have to be compensated by design: e.g. diesel soot filters need high porosity for function but this porosity results in low strength. To protect the ceramic filter against vibration in the exhaust gas system a fiber surrounding is used as damping material. For this application thermal shock resistance and chemical stability are the main requirements. The missing strength can be compensated.

Successful selection, not only of ceramic materials, is the optimal consideration of different properties like mechanical, chemical, thermal and tribolocical properties and has to consider the producibility and costs as well.

2 Structural ceramic materials

Ceramic materials can be divided into two groups concerning their atomic bonding:

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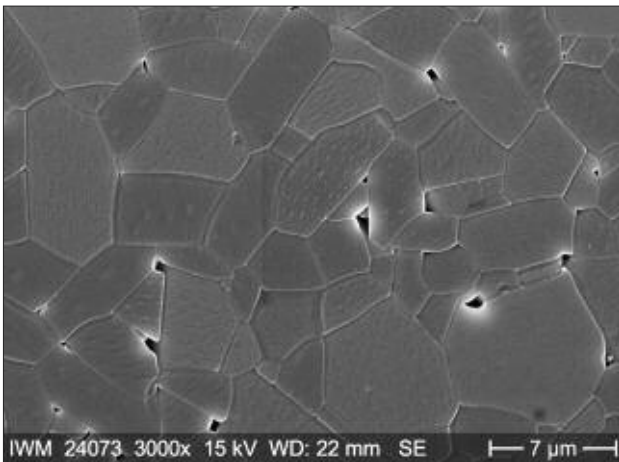
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Fig. 1
Microstructure of 99,7 % Al_2O_3 with small amount of residual pores

Fig. 2
Summer ski jump with alumina sliding components (CeramTec-ETEC)

Ionically and covalently bonded ceramics. This is mentioned because the strong covalent bonding inhibits sintering of ceramics such as silicon nitride and silicon carbide. Necessary sintering aids can decrease the application temperature and the corrosion resistance. Four common ceramic materials are selected as examples for presentation in this article.

2.1 Oxide ceramics

Alumina ceramics (based on Al_2O_3) and zirconia ceramics (based on ZrO_2) are ionically bonded ceramic materials which can be sintered with high purity without any additives. Strictly speaking alumina and zirconia are general terms for two wide classes of materials defined mainly by their chemical composition but also by their fineness of grains. Alumina and zirconia are chemically stable in oxidizing and reducing atmospheres up to high temperatures. The main disadvantage is their low thermal shock resistance.

2.1.1 Alumina (Al_2O_3)

Alumina is one of the most applied class of technical ceramics. Applications started with electrical insulators and with the beginning of the computer age as chip carrier and is nowadays part of our everyday life. In water taps alumina gaskets allow hot and cold water mixing without dripping over a long time. As hip joint endoprosthesis alumina combines wear resistance with biocompatibility. Alumina ceramics can be characterized chemically by the content of SiO_2 as glassy phase from

0 to 8 % and some impurities, in particular sodium. The glassy phase helps sintering and allows firing at lower temperatures, thus saving energy and making the components cheaper. If high strength is required pure and fine grained qualities are the best choice. In corrosive environments the glassy phase becomes critical because of lower chemical stability, but for sand blasting abrasion there are some advantages.

2.1.2 Zirconia (ZrO_2)

Zirconia ceramics is characterized by high strength at room temperature combined with high fracture toughness and a moderate Young's modulus. These properties are based on a microstructure hallmarked by different zirconia crystal phases. Because pure zirconia transforme, during cooling from sintering, at about 1170 °C from the tetragonal to the monoclinic crystal structure combined with a volume expansion of 5 % the ceramic would be destroyed by residual stresses. It has been found that some oxides like CaO, MgO, Y_2O_3, or Ce_2O_3 can be dissolved in the ZrO_2 lattice resulting in an "alloy" where the metal ions substitute zirconium ions on the same lattice site. The amount of the so called doping or stabilizing oxides determines the resulting amount of monoclinic phase in the ceramic and thus, the properties.

Zirconia is named by the nature and amount of the doping elements as yttria-doped zirconia (Y-ZrO_2), magnesia doped zirconia (Mg-ZrO_2) and so on. The amount of stabilization aid can also be found in the

ceramic name like fully stabilized zirconia FSZ or partially stabilized zirconia PSZ. Best strength is found for yttrium stabilized zirconia with an Y_2O_3 content of 3 mol-%. This material is commonly used for mechanical applications and also for implants and often has a small amount of alumina as second phase. The remaining content of monoclinic phase results in residual stresses and some micro-cracks which determine the fracture toughness.

An important fact for the designer to know is that the excellent strength strongly decreases with temperature (see above), which limits applications at high temperatures if strength is the main requirement. The low thermal conductivity of zirconia makes it useable as thermal barrier coating on gas turbines blades, where the relatively high thermal expansion reduces joining stresses between the metal blade and the ceramic plasma sprayed coating.
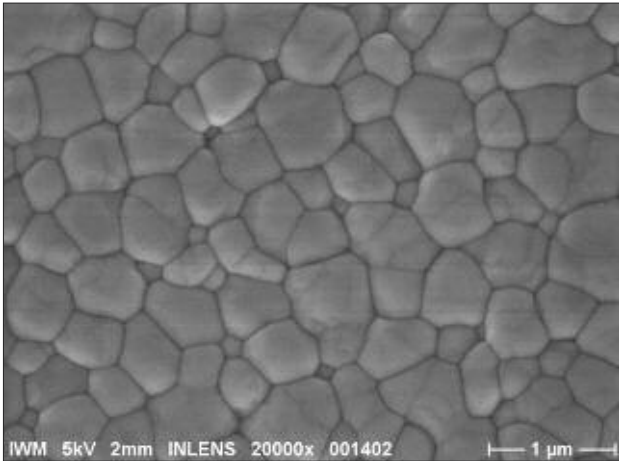

Fig. 3
Cerazur® forming tool (Doceram)

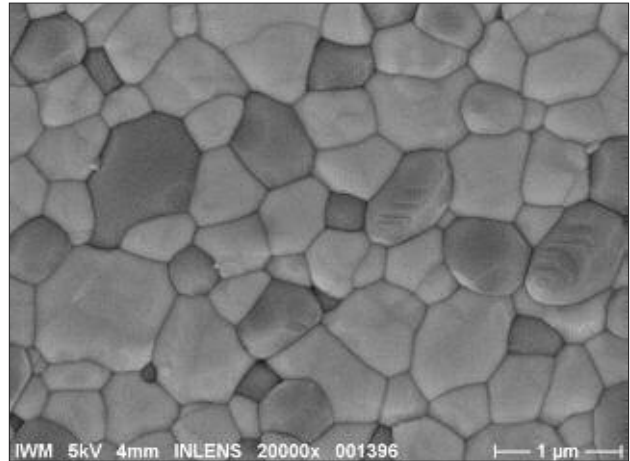Fig. 4
Fine crystalline 3Y-TZP (SEM)

Fig. 5
ZrO_2-Al_2O_3 ATZ ceramic (SEM)

Fig. 6
Ball tap with zirconia ball, alumina lining
and metal housing for corrosive media
with solid particles (CeraSystem)

On the other hand the combination of high thermal expansion coefficient and low thermal conductivity makes zirconia very sensitive to thermal shock!
A combination of zirconia and alumina improves the properties. In case of a smaller content of alumina in a zirconia matrix the material is named alumina toughened zirconia ATZ, and the other way round it is named zirconia toughened alumina ZTA.

2.2 Non-oxide ceramics
Substitution of oxygen by nitrogen or carbon results in two wide material groups of covalent bonded ceramics: nitrides and carbides. The covalent bonding is the origin for excellent properties but also for the major effort of producing and for generally higher costs. For structural applications silicon nitride and silicon carbide have a large market segments and will described here in more detail. In particular for wear applications other nitrides and carbides like TiN, BN, TiC, B_4C and mixtures of them or mixtures with other ceramics such as alumina are of special interest. An example is the material Al_2O_3-TiC/TiN used for cutting tools.

Application of non-oxide ceramics like SiC and Si_3N_4 is limited by oxidation and reactions of silicon with metals forming silicides (i.e. transition metals). Oxidation results in the formation of a SiO_2 surface hindering further oxygen diffusion and oxidation depending on thickness. The growth rate of the protective layer decreases with time. But in combination with corrosive environments elements such as alkalis react with SiO_2 and can increase the oxygen diffusion coefficient and thereby also the growth rate of the SiO_2 layer. The stability of Si_3N_4 depends on temperature and nitrogen partial pressure. In a pure N_2 atmosphere Si_3N_4 will decompose completely at temperatures above 1800 °C.
In exhaust gas (e.g. in gas turbines) consisting mainly of CO_2 and H_2O a strong decomposition of Si based ceramics is observed, explained by reactions with water steam atmospheres at temperatures above 1300 °C.

2.2.1 Silicon carbide (SiC)
With the discovery of silicon carbide at the end of 19th century technical innovations started revolutionizing many industrial sectors. The synthesized material based on sand and carbons has very high hardness and wear resistance, high thermal conductivity, low thermal expansion and density and can be manufactured with high strength. It is used as abrasive, refractories, heaters, burners and heat exchangers up to structural elements. Combined with carbon fibers CSiC can be used as brake disc for extreme applications.

The different ceramic materials within the group of silicon carbide are described by their manufacturing method and are often named using acronyms. SSiC means sintered silicon carbide and is characterized by a glassy sinter phase. Such materials are also named as LPSSiC: liquid phase sintered silicon carbide. HPSiC is a hot pressed silicon carbide and HIP a hot isostatic pressed type. Both materials (HPSiC and HIPSiC) can be produced with decreased contents of sinter additives but need an expensive technology and processing temperatures of about 2000 °C. The hot isostatic pressing technology (HIP) allows producing ceramic materials with densities of nearly 100 %.

SiSiC is produced by infiltrating a SiC-C green compact with molten silicon after the initial forming process. Silicon infiltrates the green compact by capillary forces, reacts with carbon, forming small secondary SiC grains and fills all pores. The resulting composite structure has a microstructure (Fig. 7) with large primary SiC grains, small secondary SiC grains and silicon. In view of the melting temperature of silicon (1410 °C) and the soft-

ening temperatures of the sinter additives the application temperature is limited.

For extremely high temperatures an additive free pure type can be produced by evaporating smaller grains followed by recrystallization at temperatures above 2200 °C. The so called recrystallized silicon carbide RSIC is characterized by open porosity, medium strength without a significant drop at higher temperatures.

2.2.2 Silicon nitride (Si$_3$N$_4$)

Silicon nitride is like silicon carbide a synthetic material and is the youngest of the here presented ceramic materials. Starting as refractory material in the 1950's silicon nitride was continuous developed and modified to a multitude of adapted materials. Sintering and reaction with Al$_2$O$_3$ re-

sults in SiAlONs which will not be described here.

The strong covalent bonding demands also for Si$_3$N$_4$ sintering aids in order to produce dense materials with improved strength. As described for silicon carbides the group of Si$_3$N$_4$ materials is also named according their manufacturing method as SSN, HPSN, HIPSN with similar influence of the sinter additives on microstructure and material properties. As an example in Fig. 9–10 it can be seen that the grain size of hot pressed Si$_3$N$_4$ (HPSN) is finer than of SSN. A material of high purity without sintering additives can be produced by shaping a green body of silicon powder and firing in a nitrogen atmosphere. An advantage of shaping silicon is the reduced wear of molds compared to the hard silicon nitride powder. During firing silicon
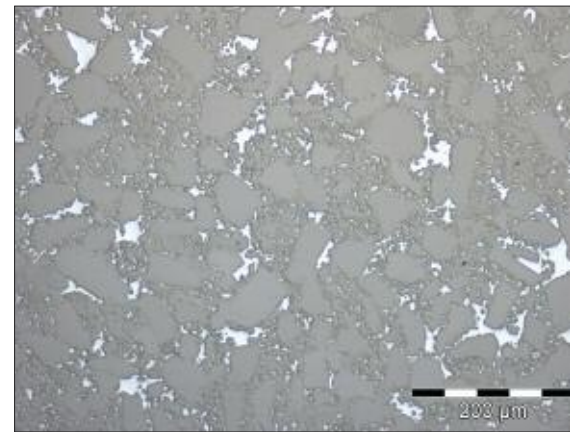

Fig. 7
Microstructure of SiSiC (LM)

reacts with nitrogen forming Si$_3$N$_4$. Such materials are called RBSN reaction bonded silicon nitride and are characterized by
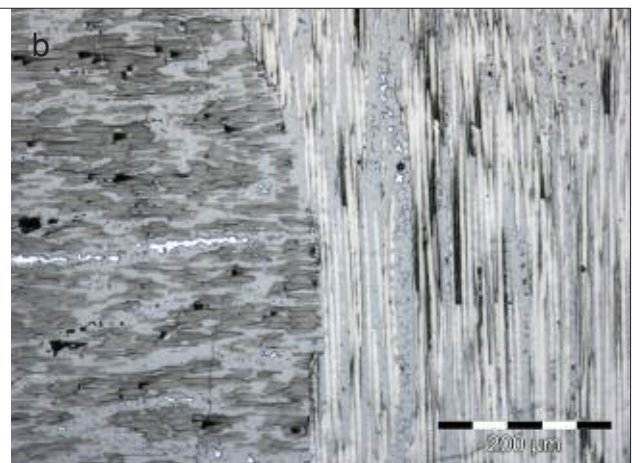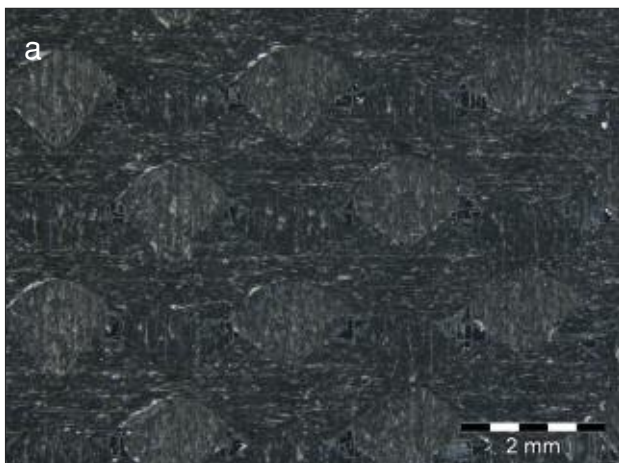

Fig. 8 a, b
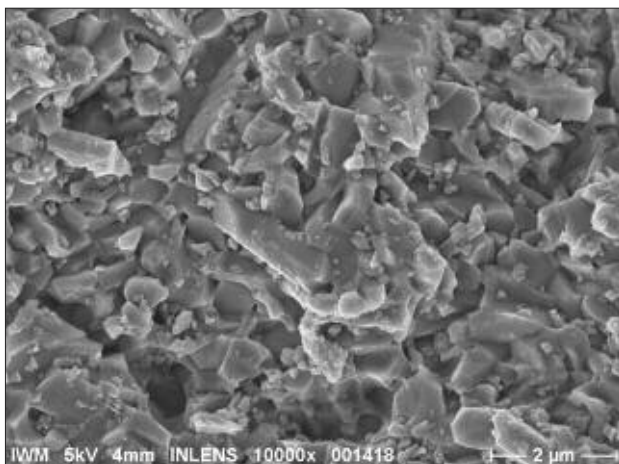Microstructure of CSiC (LM) in two directions

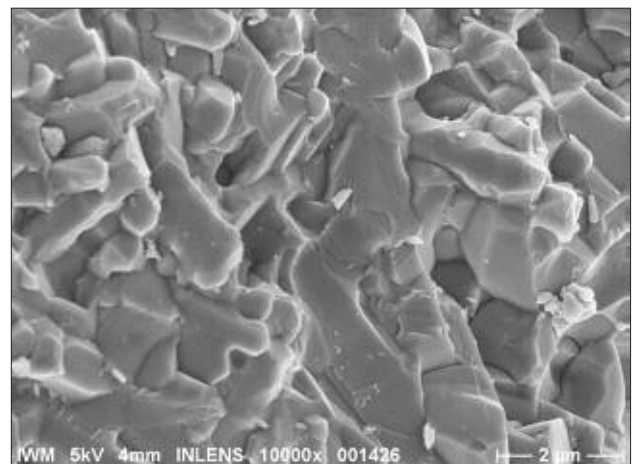Fig. 9
Fracture surface of HPSN
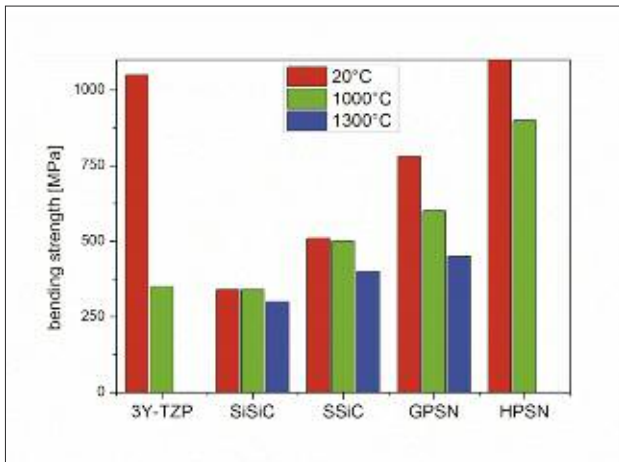

Fig. 10
Fracture surface of SSN

Fig. 11
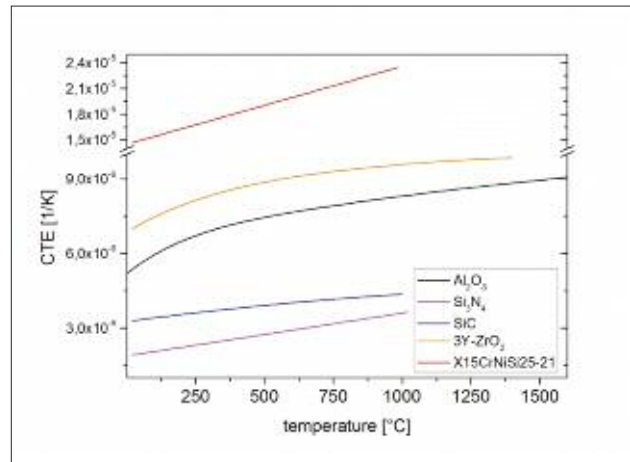Strength as function of temperature (schematically)

Fig. 12
Coefficient of thermal expansion α as function of temperature (schematically) [3]

open porosity and a reduced strength without drop up to 1200–1400 °C.

In the last decades silicon nitride materials have become more and more important and have occupied new areas of application in comparison to other ceramic materials. Today the market share is estimated as 5–10 % [2].

3 High temperature properties

In the first section of this series [1] the fundamentally different strength behavior of ceramic materials compared to metals was described. It was pointed out that the strength of a component depends on manufacturing and on size. Therefore tabulated strength data of samples can only be seen as orientation values and only for short term loading. Strength depends on defects, often surface cracks. Thus the finishing of samples and components play a major role. If it is not possible or affordable to polish a surface the strength will be reduced. Additionally most data are determined at room temperature, but the strength partially has strong temperature dependence. High temperature strength data can hardly be found. For a first orientation some data are collected below.

Not only for high temperature applications, but also for some joining techniques like shrink wrapping or brazing, thermo-physical properties such as coefficient of thermal expansion α, thermal conductivity λ, specific heat c_p are essential for stress simulations and reliability calculations.

Differences in thermal expansion of joining partners result in stresses during temperature changes. Large components can have different local transient temperatures depending on thermal conductivity. Combined with strong thermal expansion this can result in large stresses. Especially thermal cycling can become critical for some ceramic materials. To describe the thermal shock resistance of dense ceram-

$$R1 = \frac{\sigma}{\alpha \cdot E}$$

$$R2 = \frac{\sigma \cdot \lambda}{\alpha \cdot E}$$

ic materials special parameters have been created as R1 and R2.

R1 is a parameter which describes the sensitivity of a sudden thermal change at the surface of a component. The strength σ of a material should be high and the Young's modulus E and the coefficient of thermal expansion α should be low. In case of a longer through heating the thermal conductivity λ is included and R2 results. The mathematical description of thermal shock will not be continued here. It is important to know that thermal shock sensitivity depends on properties described here, but also on component size and in particular microstructure. The microstructure of thermal shock resistant refractory materials are characterized by large grains, pores and micro cracks

which can stop growing cracks before they become critical. Because of such microstructures the strength of refractories is relatively poor.

Because the properties in the parameter R1 and R2 are temperature depending thermal shock at higher temperature (e.g. molten steel flowing into a ceramic nozzle) is not the same as at lower temperatures (e.g. cooling a component by blowing air). Designer can use and adapt heat flow in or out of a ceramic component to reduce thermal induced stresses. Simulations with FEM give inputs where to insulate a component during heating up to control thermal distribution and thermal expansion in the component.

4 Summary

In the integrative design process different ceramic materials can be selected to achieve the needed properties at the right place. Often a combination of materials ("marriage of materials") is the road to success and will be described in following issues. For mechanical engineers the mechanical and thermo-physical properties are usually considered to be most important. Therefore these properties are in focus of this article. But for many applications other properties such as corrosion resistance or biocompatibility, wear resistance or friction behavior can of course be much more important and has to be integrated into the design process as well. As an example aluminium titanate, a material with poor room temperature strength of only about 30 MPa but an

excellent corrosion and thermal shock resistance can be used as riser tube for molten aluminium. In order to include costs in the design process, the user of ceramic components has to discuss with the manufacturer at an early stage. For the costs of ceramic components the powder costs are (except for very large components) of little importance although they cover a wide field from 2 EUR/kg for 92 % pure alumina to 100 EUR/kg for 99,99 % Al_2O_3, 3Y-TZP, ATZ or Si_3N_4. In contrast to most metal materials costs for the initial forming process and firing of the components have to be added. Because of this it is very helpful for designers to know the basics of the ceramic manufacturing process to take not only material alternatives into consideration, but (in time) also the manufacturing alternatives. Since normally special molds have to be manufactured for initial forming processes the cost of a ceramic product depends strongly on the lot size. But the major part of the costs falls on final shaping (grinding, polishing, lapping) where diamond
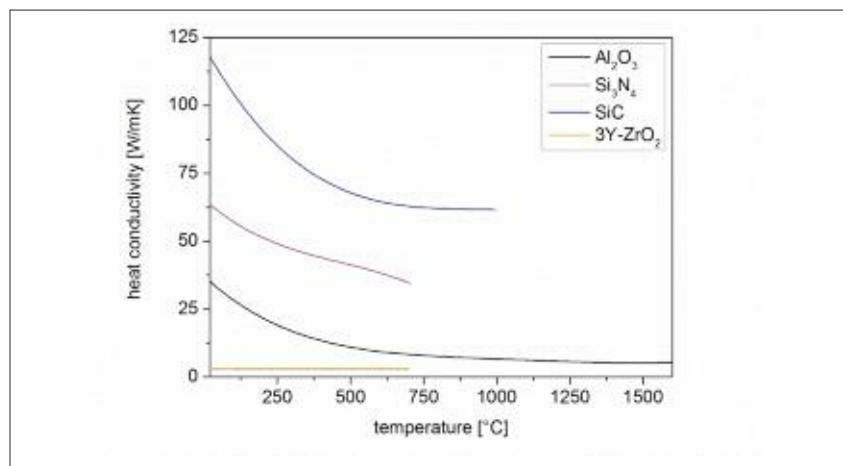

Fig. 13
Thermal conductivity λ *as function of temperature (schematically)*

tools or diamond abrasive grains have to be used.

The success of a product depends on many aspects in the design process. The right choice of a material or a combination of materials is only one aspect. Thus our series will be continued.

Acknowledgement
The microstructure pictures were made in own lab by *Cornelia Hohlstein*. We take the opportunity to say thank you to her as well as to our industrial partners for appropriate photos of components.

References

[1]   Pfaff, E.; Maier, H.R.: Product and system innovation based on integrative design with ceramics. Ceramic Applications 1 (2013) [1] 38–44

[2]   Hermann, M: Siliciumnitridwerkstoffe, in: Technische Keramik. 2nd Ed. Essen 2009, 293–330

Remark from the editor:
This series „Product and System Innovation Based on Integrative Design with Ceramics" will be continued with following topics:
„Marriage of Materials" (joining of ceramic/ceramic and ceramic/metal)
„Reliability Analysis of Ceramic Components" (FEM simulationen, optimized geometries)
„Ceramic Coatings" and „Application-oriented Testing".
Additionaly the possibilites of R & D cooperation with a ceramic institute will be reflected.