Development and Application of Electrically Conductive Ceramics

Hybrid ceramics which consist of an electrically isolating matrix (Al_20_3 or Si_3N_4) and an electrically conductive minority phase (TiN) were investigated with respect to their suitability for electrical discharge machining EDM. The influence of concentration and particle size of the minority phase on the degree of percolation and the average size of electrically non-connected volumes were studied. The calculations showed that the concentration of the conductive phase can be minimised by reducing the grain size of the conductive phase. For achieving a low surface roughness by EDM, a minimum of 90 % percolation is required. By using a nano-sized TiN powder, the sintering temperature could also be reduced by several 100 °C. This reduces production costs and helps to avoid problems due to detrimental reactions between the matrix and carbon impurities. Several demonstrators were set-up and tested which were designated for harsh working conditions.

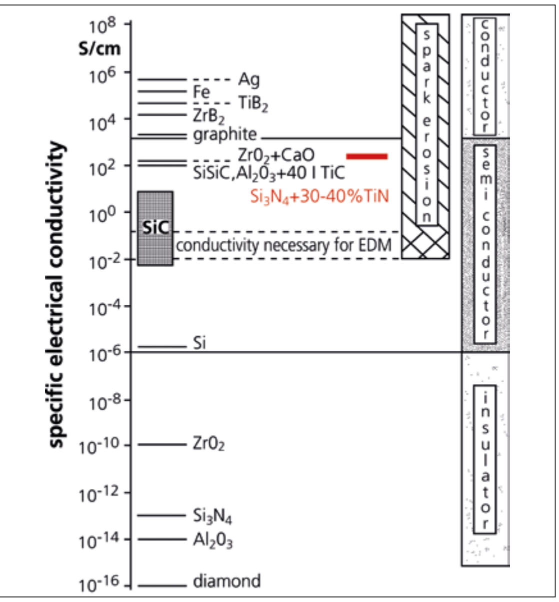

Fig. 1
Specific electrical conductivity of materials, according to [1]

Keywords
electrically conductive ceramics, EDM, multi-scale simulation, percolation, process optimisation

Introduction

Most ceramic materials have very low electrical conductivity at room temperature due to their primarily covalent or ionic bonding which does not form free electrons. There are some exceptions like graphite, semiconducting SiC or materials like $MoSi_2$ or borides which show partially metallic bonding. An overview of the electrical conductivity of selected ceramic materials is given in Fig. 1.

While in some applications of ceramics, their electrical insulation is mandatory, there are many others which either require electric conductivity or can at least benefit from it. Examples for the first case are the use of electrically conductive ceramics in electric heating or for shielding applications. An example for a benefit of electrical conductivity is the prevention of static charging.

A further important advantage of electrically conductive ceramics is the possibility to shape them by electrical discharge machining EDM, also known as spark machining, spark eroding, burning, die sinking, wire burning or wire erosion. Especially for ceramic materials, for which shaping after sintering e.g. by grinding or polishing is very tedious and expensive, or for very special shaping requirements, the possibility of EDM would be a great benefit. However, a minimum electrical conductivity of about 0,01 S/cm (equals a specific resistance of 100 Ωm) is regarded as a prerequisite for EDM processes [1, 2].

Holger Friedrich
Fraunhofer Institute for Silicate Research Center for High Temperature Materials and Design (HTL)
95448 Bayreuth, Germany
E-mail:
holger.friedrich@isc.fraunhofer.de

Rolf Wagner
Rauschert Heinersdorf-Pressig GmbH
96332 Pressig, Germany
E-mail: r.wagner@prg.rauschert.de

Kai Sauerzapfe
Alumina Systems GmbH
96257 Redwitz, Germany
E-mail: ksauerzapfe@alumina.systems

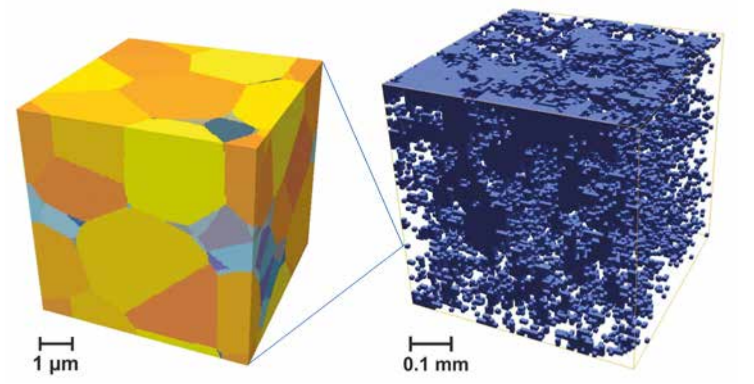

Fig. 2
3D-sketch of a representative volume element of Al_2O_3 (orang/yellow) containing TiN (blue/gray) as conductive phase (left) and simulation of non-contacted regions (blue) in a large grid at 60 % percolation (r.)

There have been different approaches to shape non-conductive ceramics by EDM based on the Assisting Electrode Method. However, there is still a long way to go, before these EDM processes will be established as a standard manufacturing process for machining both conductive and non-conductive ceramics [3].

An alternative way to facilitate EDM processing is to increase the electrical conductivity of an isolating ceramic by the addition of a second, electrically conductive phase. Usually, the content of the second phase in these hybrid materials is in the range of 30–35 vol.-%. This high amount of the additions is necessary to reach the so-called percolation threshold. It denotes the minimum content for the conductive phase to form a continuous network leading to macroscopic conductivity. However, close to the percolation threshold, there are still larger volumes which are not electrically connected. These isolated volumes pose a major problem for EDM, because they limit the achievable surface quality. Therefore, even higher amounts of the second phase are commonly incorporated in the material, with the significant drawback (depending on the intended application) that the second phase also modifies other, e.g. mechanical, properties of the matrix material. Thus, it is an apparent development goal for this approach to minimise the percentage of the conductive phase needed to reach the percolation threshold.

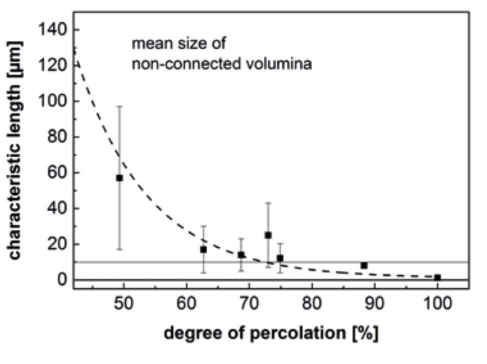

Fig. 3
Influence of the degree of percolation on the mean size of non-contacted volume

In the presented work, two important technical ceramics, Al_2O_3 and Si_3N_4, have been chosen for further investigation of the approach. The electrically conductive phases which have been selected for investigation encompassed TiN, TiC and mixtures thereof as well as $MoSi_2$ and carbon forms like graphene or carbon nanotubes which are usually recommended as additives. Thermodynamic calculations and microstructural simulations were used in order to minimise the experimental effort and to demonstrate the potential of particle size and shape adaptations on the percolation threshold. Besides these general tasks, demonstrators were developed, in which these composites have been tested in aggressive working conditions.

Material development

The addition of a second phase can lead to detrimental chemical reactions during sintering. Therefore, the thermodynamic stability of potential combinations of Al_2O_3 and Si_3N_4 with electrically conductive phases was calculated using the thermodynamic data base FactSage™. Calculations were performed with TiN, TiC, carbon and $MoSi_2$ as additional phases in the temperature range of the respective sintering processes. It was confirmed that for both cases, Al_2O_3 and Si_3N_4, any sort of carbon should be omitted due to gas forming reactions. Thus, TiC and carbon structures were excluded from further investigations, although technical adaptations like pressure assisted sintering under defined atmospheres can minimise these reactions.

In addition, these calculations showed that residual carbon which is formed during debinding has to be carefully controlled.

Microstructural simulations on the percolation behaviour as a function of grain size ratio of two-phase ceramics were conducted using special algorithms developed at HTL [4]. The probability of electric connection between different faces of a small Representative Volume Element (RVE) was used to construct the percolation network in a large grid which represents a material volume in the range of some cubic millimetres. To account for the statistical nature of real microstructures, typically ten different small RVEs were generated for a special composition (volume content, grain size and shape), and the resulting percolation grades were averaged.

Fig. 2 shows an example for an RVE representing an Al_2O_3/TiN microstructure (l.) and the corresponding large grid for percolation assessment (right). The RVE was formed from a Voronoi tessellation of randomly distributed particles of both phases with preset size distributions. The blue cubes (Fig. 2, r.) represent regions isolated from an electrode contacting the bottom side of the grid. It is obvious that large non-contacted areas, e.g. as seen at the left top corner, would be problematic for EDM.

This topic was studied quantitatively by deriving the average size of non-contacted regions for different degrees of percolation (Fig. 3). It was concluded that a degree of percolation above 90 % should be achieved to avoid large isolated regions during EDM.

In order to achieve a high degree of percolation with a minimum concentration of conductive phase the ratio of particle sizes between conductive and matrix phase was varied (Fig. 4). It can be seen that the ratio of particle sizes drastically affects percolation. At a particle size ratio of 0,27, 100 % percolation is achieved with 15 vol.-% of conductive phase whereas 30 vol.-% are required for a particle size ratio of 1 (Fig. 4).

In order to verify these results, a nano-sized TiN-powder and a micron-sized TiN-powder were used to produce Al_2O_3–TiN composites. One requirement for exploiting the benefits of nano-scaled particles is their homogenous dispersion in the green body. Furthermore, segregation during sintering has to be avoided. Examples of a successful realisation are shown in Fig. 5. Due to the higher sintering activity of the fine TiN-particles, a second benefit could be used: Fig. 6 shows the sintering curves of a composite with nano-scaled TiN in comparison to micro-scaled TiN. The onset of sintering as well as the main densification step are shifted to much lower temperatures for the nano-scaled TiN. This also leads to less grain coarsening, as can be seen in Fig. 5, and lower cost. Additionally, undesired reactions of residual carbon or impurities of TiC with the matrix, which occur notably above 1500 °C, can be reduced.

According to thermodynamic calculations shown before, carbon leads to undesired reactions with the matrix during sintering and the formation of volatile gases. If these reactions take place, after pores have been closed, the formation of gases will lead to swelling and crack formation.

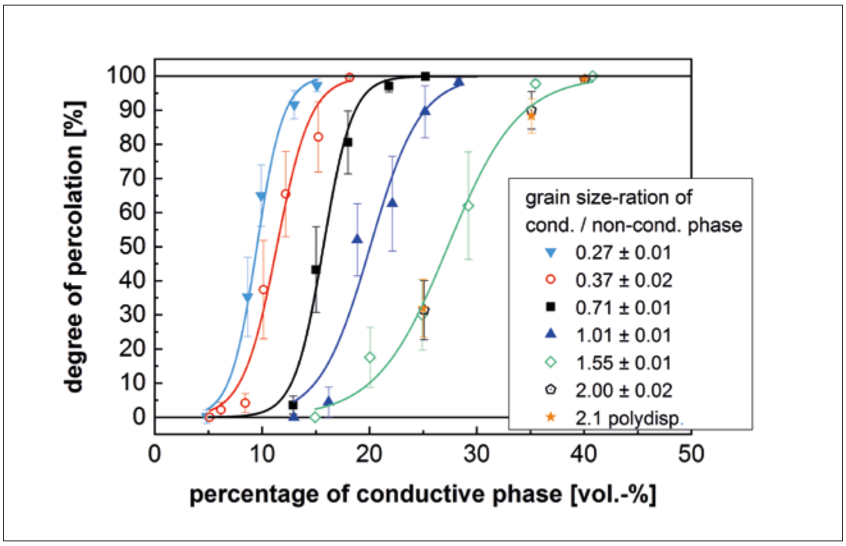

Fig. 4
Influence of the particle size ratio of the electrically conductive to the electrically isolating phase on the degree of percolation for equiaxed particles

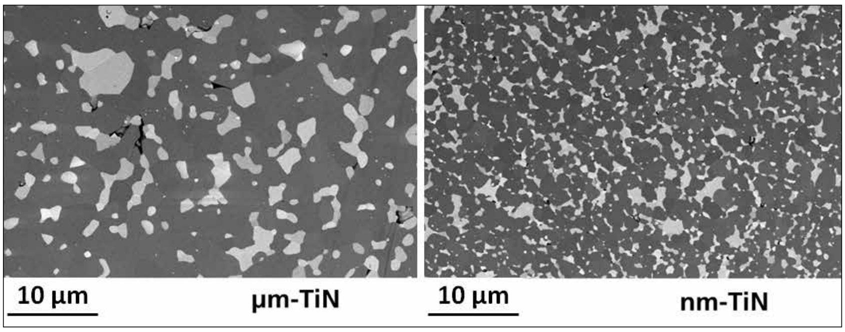

Fig. 5
SEM image (Energy Selective Backscattered (ESB)-signal) of an Al_2O_3–TiN composite with micro-sized TiN (l.) and nano-sized TiN (r.) particles after sintering; concentration of TiN (bright phase) was 19 vol.-%

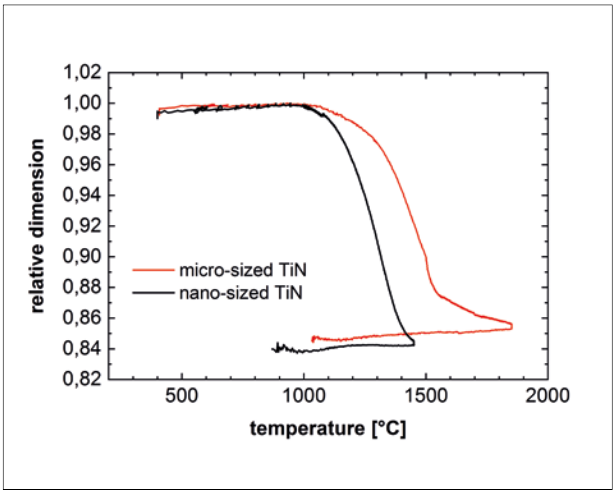

Fig. 6
Sintering curves of Al_2O_3-composites with nano-scaled TiN in comparison to micro-scaled TiN as second phase

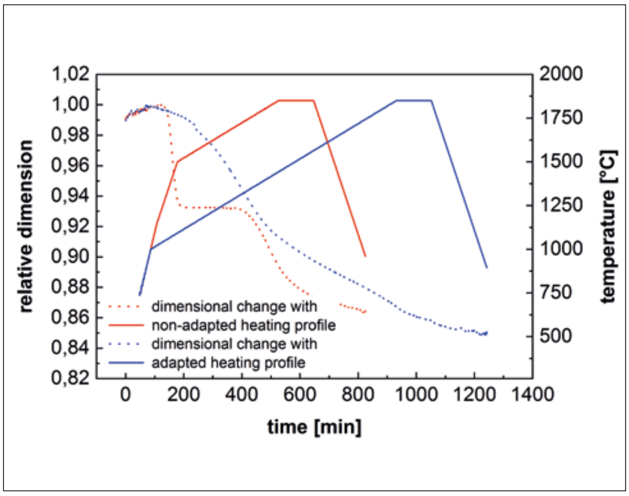

Fig. 7
Shrinkage and corresponding time-temperature curves for Al_2O_3–TiN composites for the cases of a non-optimised heating cycle with swelling (indicated by black circle) and an optimised time-temperature curve

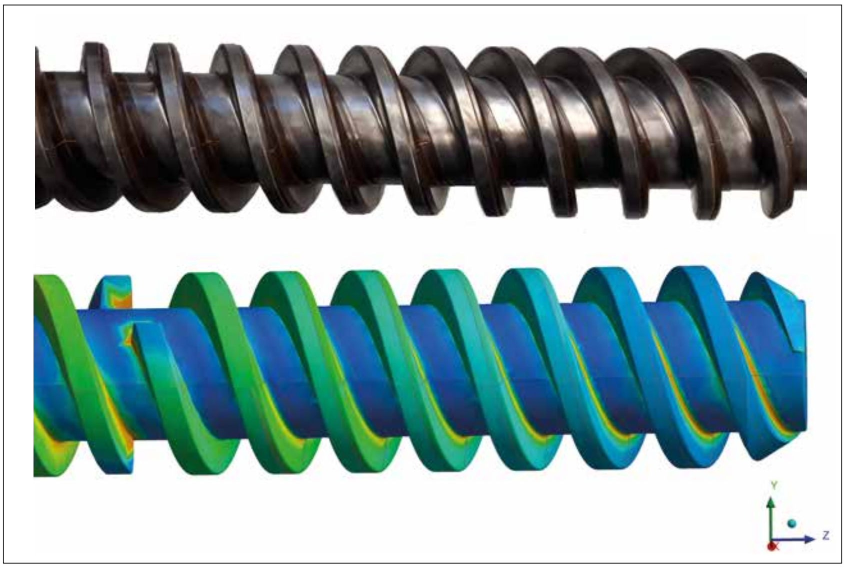

Fig. 8
Extrusion screw with ceramic armour plates and calculated stress distribution under application conditions

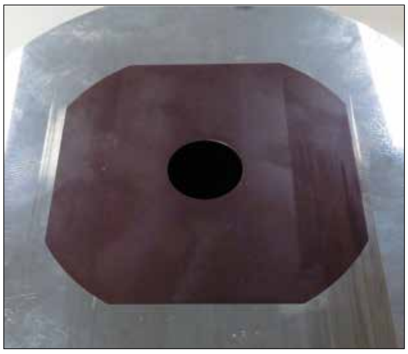

Fig. 9
Inlet for dry pressing die

This effect can be seen, for example, in the sintering shrinkage curve shown in Fig. 7. After an initial sintering shrinkage up to a temperature of about 1500 °C, a temporary plateau is reached. During this plateau, swelling counteracts the shrinkage of the material. This detrimental effect can be prevented by adapting the heating cycle using lower heating rates. Due to the longer heating time, all residual carbon has been decomposed at conditions, where the pore network was still open and allowed for easy gas permeation. Swelling could be prevented. The carbon originated from organic processing additives, which have been pyrolyzed during the debinding step.

Debinding under oxygen could also be performed in order to minimise the amount of residual carbon. However, a side effect would be the surface oxidation of TiN particles forming TiO_x which would have a negative effect on the electrical conductivity – especially as these oxide layers would develop grain boundary resistances inside the final component.

Application studies

Below several application examples will be presented for the composite material Si_3N_4–TiN. A special focus has been set on an extrusion screw for particle filled polymers, which is customarily made of steel. Due to the combination of high temperature, high pressure and corrosive atmosphere as well as abrasive components, severe wear during use of this component is a problem. So a more resistant solution based on ceramics was developed. The choice of design was based on thorough mechanical testing and thermomechanical simulation using ANSYS at Alumina Systems/DE. Based on these results, both a full-ceramic and an attachable set-up which had been developed before had to be abandoned.

Finally, a design, which uses protective armour plates at the critical positions of the screw, was proposed. The shape of the amour plates was fine-tuned considering local stress fields. Besides the much lower risk of failure, cost aspects as well as the possibility to replace single plates supported the decision to use individual armour plates. A key requirement for such a design was the good machinability of the ceramic material which allowed for high tolerance tightness. Besides the general design and choice of material, a way on how to attach the ceramic material to the metallic screw had to be developed. This included both, the kind of connecting material which would be able to withstand the application conditions as well as a suitable process to adhere the ceramic plates to the metal screw at the necessary high level of accuracy. The final design is shown in Fig. 8. It has been set up and running without any problems in the application.

Besides the development of the extrusion screw, the new materials have also been used for further demanding applications. Some of those are shown in Figs. 9–10. A dry pressing die for navels used e.g. in the textile industry has been prepared by EDM and run in production.

As another example, a glass funnel has been produced and run successfully for the production of round glass flacons. For the production of the funnels, standard machining has been applied demonstrat-

Fig. 10
Inlet for glass flacon production

ing the very good machinability of the green material.

Further applications have been spinnerets for the production of ceramic fibres at HTL. In this case, holes with a diameter of 100 µm could be introduced without problems. Additionally, tool inserts and tools for dry pressing have been produced and are currently under testing.

Summary

The addition of a second phase is a suitable way to make electrically insulating ceramics conductive. One benefit is that EDM methods can be used for shaping of sintered ceramics. Thermodynamic calculations were applied in order to find appropriate materials which do not show detrimental reactions with the matrix.

As a result, carbon containing phases were excluded due to gas forming reactions with Al_2O_3 and Si_3N_4 during sintering. The amount of second phase which is necessary to establish a well-conductive connected network was calculated by help of microstructural simulations. It could be shown that for a percolation of less than 90 % the size of non-connected volumes is several 10 to 100 µm which would lead to a rough surface and the risk of problems during EDM.

Furthermore, following the simulation results, the amount of second phase necessary to reach 90 % percolation could be strongly reduced by using well-dispersed nano-particles in a micron-scaled matrix material. Considering alumina based composites, a further benefit of the nano-scaled raw material was the reduction of the sintering temperature by several 100 °C, leading to cost benefits and the prevention of undesired gas forming reactions. Based on these kinds of hybrid materials, several demonstrators have been produced for harsh application conditions. Examples encompassed the engineering, design and installation of a ceramic armour protected extrusion screw for particle filled polymers as well as components for pressing dies, glass forming and ceramic fibre production. Both knowledge and experience on material development and application of hybrid materials consisting of an electrically insulating matrix and an electrically conductive second phase could be gained successfully.

Acknowledgement

The authors thank the project partners for their contribution to this project. Important experimental work and simulation has been contributed by Marian Stepanyan (HTL) and Gerhard Seifert (HTL).

Financial support by the Bavarian Ministry of Economic Affairs and Media, energy and Technology/DE within the program „Neue Werkstoffe Bayern“ is gratefully acknowledged.

References

[1] König, W.; et al.: CIRP Annals – Manufacturing Technology **37** (1988) [2]

[2] Schubert, A.; Zeidler, H.; Kühn, R.; Hackert-Oschätzchen, M.: Microelectrical discharge machining: A suitable process for machining ceramics. Journal of Ceramic 2015

[3] Bilal, A.; et al.: Electro-discharge machining of ceramics: A review. Micro_machines **10** (2019) [1]

[4] Müller, T. M.; Raether, F.: 3D modelling of ceramic composites and simulation of their electrical, thermal and elastic properties. Computational Materials Science **81** (2014) 205–211