# Electric Discharge Machinable Ceramics with Oxide Matrix – Compositions, Properties and Machining Features

Manufacturing of customised ceramic components of low dimensional tolerances and complex geometrical features with lot size one is a technological and economic challenge. If additive manufacturing technologies or conventional milling from blanks cannot deliver the required component strength or accuracy electric discharge machining (EDM) of ceramics present an attractive alternative as die sinking and wire cutting processes well established in metal machining can be applied. EDM requires electrically conductive workpieces so that the available ED-machinable ceramics combine a structural ceramic matrix with a conductive second phase such as a transition metal carbide, nitride or boride. The paper aims at providing some insight on materials with alumina/zirconia and partially stabilised zirconia oxide based matrix, their properties and machining features.

#### Introduction

Due to the high hardness and abrasion resistance of dense structural ceramics machining processes final conventional machining steps such as grinding, lapping and polishing are slow and costly and should be avoided or reduced to the necessary minimum. This leads to the surging field of additive manufacturing technologies which are capable of manufacturing customized components and conventional net-shape manufacturing technologies such ceramic injection moulding or die pressing which are typically applied in mass production. Conventional manufacturing of customized parts is typically performed by machining of cold isostatically pressed blanks in the green state (e.g. hip joints) or in the white

#### *Keywords*

electric discharge machinable ceramics, conductive structural ceramics

(pre-fired) state (e.g. dental crown and bridges).

Machining can then be done by highly productive milling and turning operations, however the dimensional accuracy is limited, some geometrical features are not possible and a final machining step may still be necessary [1].

Non-conventional or hybrid machining processes such as EDM and Laser machining are documented in literature, are currently rarely applied, but may fill the remaining gap which cannot be covered by the above mentioned processes.

EDM is a more or less force-free electrothermal machining technology which is independent of the hardness of the workpiece. As the material removal is accomplished by melting or evaporation of material induced by an electrical discharge between a tool electrode and a workpiece electrode separated by a dielectric fluid (typically water or oil) it requires an electrically conductive workpiece [2].

Conventional oxide or non oxide structural ceramics, with some exceptions ( $B_4C$ , TiB<sub>2</sub>, SiSiC) are non-conductive or semiconducting. Application of EDM, therefore required the development of tailored ED-machinable materials. Typically a non conductive structural ceramic (alumina, ZTA, silicon nitride, zirconia) represents the matrix material, the electrical conductivity is introduced by a percolating dispersion of a conductive material, typically a transition metal carbide nitride or boride [3]. Recently also low dimensional carbon allotropes such as graphene or carbon nanotubes were

Frank Kern Universität Stuttgart, IFKB 70569 Stuttgart

E-mail: frank.kern@ifkb.uni-stuttgart.de

Tab. 1

Mechanical properties and electrical conductivity of hot pressed ZTA-based ED-machinable ceramics

Material***	Hardness HV10 [–]	Young's Modulus [GPa]	Bending Strength* [MPa]	Fracture Toughness** [MPa√m]	Electr. Conductivity [S/m]	Ref.
17ZTA1.5Y-24TiC Dimacer®	1960	399	600	5.2	5000	[10]
17ZTA1.5Y-28TiC	1970	365	750	4.7	9500	[13]
17ZTA1Y-28NbC	1870	375	875	4.9	65 000	[11]
10ZTA0Y-28TiN	1720	385	730	4.9	40 000	[14]

\* four point bending (20/10 outer/inner span)

\*\* ISB (indentation strength in bending) method

\*\*\* aZTAbY-cED denotes a ZTA with: a [vol.-%] zirconia, stabilised by b [mol-%] of yttria and c [vol.-%] of electrically conductive dispersion

tried [4]. The lower conductivity threshold to make machining feasible in principle is 1 S/m, our own results show that several orders of magnitude more (~104 S/m) are necessary to guarantee good machining results) [5].

The materials designed for EDM were Si<sub>a</sub>N<sub>4</sub>-TiN and Y-TZP-TiN, later on materials such as Y-TZP-WC, Y-TZP-NbC and ZTA-TiC were introduced aiming at improving different features such as increased hardness, toughness or strength or better machinability [6-10]. In various publicly funded projects the high performance ceramics group at IFKB in Stuttgart focused on developing new ZTA-NbC [11] and TZP-WC [12] materials. Complementary and equally important to the materials development suitable ED-machining parameters had to be elaborated, this was done in joint DFG projects with WZL/RWTH Aachen.

#### ZTA based materials

The first ZTA based materials were developed in a AiF-ZIM Project in cooperation with Leroxid GmbH. The target application were tool inserts for injection moulding of abrasive feedstocks such as particle or glass fibre filled polymers, or powder injection moulding feedstocks containing ceramics or metals. These inserts should protect the metal moulds in locations where high wear was expected due to high relative speed or change in flow direction. As these moulds experience some thermocycling the coefficients of thermal expansion of the steel mould and the ceramic inserts should not differ too much to avoid build-up of compressive residual stress or gaps between mould and insert depending on the geometric conditions. Hardness was also important whereas the strength and toughness was not emphasized as no free standing structures were expected. The mechanical properties of various ED-machinable ZTA materials are summarised in Tab. 1.

The toughness of all these ZTA based composites is moderate (~5 MPa $\sqrt{m}$ ), the hardness (17–20 GPa) depends on the type and amount of the second phase. Highest hardness was achieved with TiC followed by NbC and TiN. The improvement of processing parameters (compare the first two ZTA-TiC materials) is clearly visible in improved strength. ZTA-NbC generally showed the best strength values among all ZTA based materials.

Fig. 1 shows a typical microstructure of 17ZTA1.5Y-24TiC (a. 24 TiC coarse = Dimacer®) and 17ZTA1.5Y-28TiC (b. 28 TiC fine). The three constituents are clearly visible. Titanium carbide grains are bright grey the oxide matrix consists of microsize alumina (black grains) and submicron zirconia grains (white grains). Using more and finer TiC obviously not only decreases the



#### Fig. 1

Microstructure of ZTA-TiC, SEM images of polished and thermally etched surface: a) 17ZTA1,5Y–24TiC (Dimacer®), average TiC grain size 2,5 μm; b) 17ZTA1,5Y–24TiC, average TiC grain size 1 μm



Fig. 2

SEM image (SE) of ED-machined ZTA-TiC materials:

a) 24 ZTĂ coarse (Dimacer®) WEDM surface;

b) 28 ZTA fine (contains 28 % TiC with 1 µm grain size) WEDM surface;

c) 24 ZTA coarse (Dimacer<sup>®</sup>) die sinking surface;
 d) 24 ZTA coarse (Dimacer<sup>®</sup>) die sinking cross section

grain size of the dispersion but also of the matrix. These modifications had a moderate effect on mechanical properties but a drastic effect on electrical conductivity and ED-machining characteristics. Fig. 2 shows the surfaces and cross sections of EDM machined ZTA-TiC. The classical Dimacer®material (a. 24 ZTA coarse) machined by wire EDM shows a foamy surface structure with coarse microstructure features. The ED machined surface of the ZTA material with a larger fraction of fine grain TiC (b. 28 ZTA fine) shows still foamy surface structure but much lower roughness. The material machined by die sinking (c. and d. 24 TiC coarse DS) show a typical splatlike surface structure which is originates from the overlap of the discharges. The cross-section (d.) shows that the surface is covered with a very thin layer of molten and re-solidified material and that the fine crack network visible in the surface does not penetrate into the bulk.

The retention of strength after machining is a critical issue as the EDM process may lead to surface defects, residual stress and cracks. Landfried investigated the strength of ZTA-TiC during different stages of WEDM [15]. The strength of the pristine material (800 MPa) was reduced during the main cut and the first trim cut to 600 MPa, two additional trim cuts led to a recovery of strength (700 MPa). Even more important was the evolution of the Weibull modulus. While the pristine material and the materials after main cut and first trim cut had rather poor Weibull moduli (4-5), the second and third trim cut increased the Weibull modulus to 9 (2<sup>nd</sup> trim) up to 20 (3<sup>rd</sup> trim). Evidently the existing defect population in the material is

replaced by a very homogeneous population of machining induced defects.

The surface quality in terms of mean surface roughness Ra of ZTA-TiC materials cannot be drastically reduced by the trimming operations [16]. The main cut leads to roughness values of Ba = 2.5 um. application of three further trim cuts reduces the roughness to  $\sim$ 1.7 µm. The reason for this behaviour is the ternary composition. Alumina melts at ~2050 °C and evaporates at ~3000 °C. Zirconia and titanium carbide have considerably higher evaporation temperature. Therefore the material removal mechanism in ZTA-TiC is dominated by evaporation which leads to the foamy surface structures shown above (Fig. 2 a, b). Trimming operations with lower energy input remove and reproduce a foamy structure as the material removal mechanism does not change.

#### Zirconia based materials

While the ZTA based materials offer high hardness and abrasion resistance some applications require higher strength and damage tolerance. This field can be covered by materials such as TZP-WC. First results using commercially available coprecipitated 3Y-TZP materials as a matrix and adding 24-32 vol.-% tungsten carbide lead to materials with extremely high strength but a toughness which is moderate and very similar to the 3Y-TZP starting powder. In the frame work of a DFG project new composite materials based on rare earth co-stabilised TZP materials led to materials with even higher strength and improved toughness (Tab. 2). Properties of commercially available Y-TZP-35TiN materials are close to 3Y-TZP 28 WC.

Fig. 3 shows the microstructure TZP-WC materials in comparison. 3Y-TZP 28 WC made from Tosoh 3YSE and a nanoscale tungsten carbide (Högenäs DN4.0) consists of zirconia grains of ~500 nm size

Tab. 2

Mechanical properties and electrical conductivity of hot pressed TZP-based ED-machinable TZP-WC ceramics

Material***	Hardness HV10 []	Young's Modulus [GPa]	Bending Strength* [MPa]	Fracture Toughness** [MPa√m]	Electr. Conductivity [S/m]	Ref.
3Y-TZP 28 WC	1630	290	1300	5,5	90 000	[16]
1.5Y1.5Nd-TZP 28 WC	1570	290	1400	8,7	45 000	[12]

\* four point bending (20/10 outer/inner span)

\*\* ISB (indentation strength in bending) method

\*\*\* aZTAbY-cED denotes a ZTA with: a [vol.-%] zirconia, stabilised by b [mol-%] of yttria and c [vol.-%] of electrically conductive dispersion



#### Fig. 3

Microstructure of different TZP-WC materials, thermally etched in H<sub>2</sub>: a) 3Y-TZP – 28 vol.-% WC (commercial 3Y-TZP starting powder); b) 1.5Y-1.5Nd-TZP – 28 vol.-% WC (co-stabilised in house)

and a nanoscale (~100–200 nm) WC dispersion (note the different magnifications). TZP materials based on the co-stabilised 1.5Y-1.5Nd-TZP has a considerably finer grain size. The finer TZP microstructure lowers the electrical conductivity, the much higher transformability of the YNd-TZP boosts toughness and strength.

In ED-machining the TZP-WC materials differ strongly from the ZTA based materials. Both zirconia (~2700 °C) and WC (2730 °C) melt/decompose at very high temperatures. The dominant material removal mechanism is therefore melting. This can be seen in SEM images of ED-machined TZP-WC composites.

The cross section reveals a  $1-2 \mu m$  thick molten layer which can be clearly distinguished from the bulk material below. This layer contains bright round WC particles embedded in a layer of zirconia. Evidently only a part of the molten material is removed and a part re-solidifies on the surface. The residual cooling stresses and the volume increment of the phase change seem to put this layer under tensile stress so that cracks initially perpendicular to the surface are generated. These cracks extend  $\sim$ 5 µm into the material. In some cases the cracks may even lead to component failure. In order to solve this problem the recipes were modified by increasing the WC content to 36 vol.-% and by addition of up to 10 vol.-% alumina. WC addition increases the hardness, increases the strength but slightly reduces toughness. Alumina addition in fractions > 5 % leads to a reduction in toughness while the other parameters were little affected [12]. TZP-WC materials required a re-design of the machining process to retain as high strength as possible [17]. Initially the machining strategy adopted from metal machining was applied. After a first main cut with high energy which was designed for high cutting speed a subsequent trimming operation was applied to smoothen the surfaces and remove the



Fig. 4 Surface structure and cross section of Wire ED-machined 3YTZP-28WC material

#### COMPONENTS

## **TECHNOLOGY INSIGHTS**



Fig. 5 Images if a ED-milled internal thread

machining affected zone. It turned out that this strategy was not suitable to retain the high strength of the materials. The strength of 1.5Y1.5Nd-TZP/28WC material studied declined from 1410 MPa to 814 MPa after the main cut. The trimming operation further reduced the strength to 680 MPa rather than improving it as expected. The machining cycle was changed, with a main cut with lower energy input the strength still declined to 833 MPa, the subsequent trimming operation improved the strength to 933 MPa. Similar to the results obtained with ZTA-TiC properly ED-machined showed a drastically reduced scattering in strength as the machining process introduced a homogeneous set of surface defects.

# Components made from ED-machined ceramics.

Fig. 5 shows some features of a ED-machined ZTA-TiC (Dimacer<sup>®</sup>) material. This 0,6 mm internal thread was machined by ED-milling (A variation of the die sinking technology) into a thin plate. Such a geometry would be impossible to produce by conventional machining.

#### Summary

ED-machinable composite ceramics with an oxide matrix and an electrically conduc-

tive non-oxide dispersion open new perspectives in manufacturing of customised ceramic components with high complexity. The technology is especially attractive if conventional dry pressing and milling technologies are not capable of producing parts with the required accuracy and if the new additive manufacturing technologies such as stereolithography do not lead to components with the required mechanical properties. ZTA based materials offer high hardness and abrasion resistance but only moderate toughness and strength. They are produced from less expensive raw materials and are suitable for tribologically components such as moulds and dies. The recently developed TZP-WC-materials offer a unique combination of toughness and strength - almost reaching cemented carbides. These TZP based materials are expensive but suitable for components exposed to high stress. Electric discharge machining is possible by die sinking and wire cutting. Especially the wire cutting process requires very well adjusted machining procedures of main cut and subsequent trimming cut(s) to obtain components with high surface integrity. Typically ED-machining reduced the strength compared to the pristine ceramic material. As the machining process replaces the natural flaws by a new set of very homogeneous artificial machining induced defects the reliability of the machined components is very high. Weibull coefficients rise considerably which facilitates the lay out of design and reduced the otherwise very high coefficients of safety.

#### References

- Gadow, R.; Kern, F.: 2.06 Advanced manufacturing of hard ceramics. In: Sarin, V.K. (ed.): Comprehensive Hard Materials, Amsterdam 2014, 207–230
- Klocke, F.; & König, W.: Funkenerosives Abtragen (EDM). In: Fertigungsverfahren
   3: Abtragen, Generieren, Lasermaterialbearbeitung, Berlin, Heidelberg 2007, 3–126
- [3] Iwanek, H.; et al.: Machining of ceramics by different methods. In: Bunk, W.; Hausner, H. (eds.): Ceramic Materials and Components for Engines, Bad Honnef 1986, 417–423
- [4] Muñoz-Ferreiro, C.; et al.: Highly efficient electrical discharge machining of yttria-

stabilized zirconia ceramics with graphene nanostructures as fillers. J. Europ. Ceram. Soc. **42** (2022) [13] 5943–5952

- König, W.; et al.: EDM-future steps towards the machining of ceramics. CIRP Ann. Manuf. Technol. **37** (1988) [2] 623– 631
- [6] Bucciotti, F.; Mazzocchi, M.; Bellosi, A.: Perspectives of the Si<sub>3</sub>N<sub>4</sub>-TiN ceramic composite as a biomaterial and manufacturing of complex-shaped implantable devices by electrical discharge machining (EDM). J. Appl. Biomater. Biomech. 8 (2010) [1] 28–32
- [7] Pitman, A.; Huddleston, J.: Electrical discharge machining of ZrO,/TiN particulate

composite, British Ceram. Transactions **99** (2000) [2] 77–84

- [8] Anné, G.; et al.: Hard, tough and strong ZrO<sub>2</sub>–WC composites from nanosized powders. J. Europ. Ceram. Soc. 25 (2005)
   [1] 55–63
- [9] Santos, C.; et al.: Mechanical properties of hot-pressed Zr02–NbC ceramic composites. Int. J. of Refractory Met. and Hard Mater. 26 (2008) [1] 14–18
- [10] Landfried, R.; et al.: Development of electrical discharge machinable ZTA ceramics with 24 vol.-% of TiC, TiN, TiCN, TiB<sub>2</sub> and WC as electrically conductive phase.
   Appl. Ceram. Technol. (2013) [10] 509–518

### TECHNOLOGY INSIGHTS

- [11] Schmitt-Radloff, U.; Kern, F.; Gadow, R.: Wire-electrical discharge machinable alumina zirconia niobium carbide composites – Influence of NbC content. J. Europ. Ceram. Soc. **37** (2017) [15] 4861–4867
- [12] Walter, E.; Gommeringer, A.; Kern, F.; Influence of alumina content to mechanical properties and electric discharge machinability of zirconia (1.5Y-1.5Nd-TZP)tungsten carbide-alumina composites. J. Europ. Ceram. Soc. **43** (2023) [7] 2834–2842
- [13] Schmitt-Radloff, U.; et al.: Effects of composition on mechanical and ED-machining

characteristics of zirconia toughened alumina – titanium carbide (ZTA-TiC) composite ceramics. Procedia CIRP (2018) [68] 17–21

- [14] Gommeringer, A.; Kern, F.: Mechanical properties and electrical discharge machinability of alumina-10 vol.-% zirconia-28 vol.-% titanium nitride composites. Ceramics 3 (2020) [2] 199– 209
- [15] Landfried, R.: Funkenerosiv bearbeitbare Keramiken f
  ür den Werkzeug- und Formenbau. PhD thesis Universit
  ät Stuttgart, Aachen 2014
- [16] Gommeringer, A.; et al.: ED-machinable ceramics with oxide matrix: Influence of particle size and volume fraction of the electrical conductive phase on the mechanical and electrical properties and the EDM characteristics. Procedia CIRP (2018) [68] 22–27
- [17] Olivier, M.; et al.: Wire electrical discharge machinability and loadbearing capacity of ATZ-WC composite ceramics. Paper presented at ESAFORM 2021. 24<sup>th</sup> Int. Conference on Mater. Forming, Liège, Belgium (2021)



www.eitec-gmbh.de info@eitec-gmbh.de

We are doing things today for tomorrow