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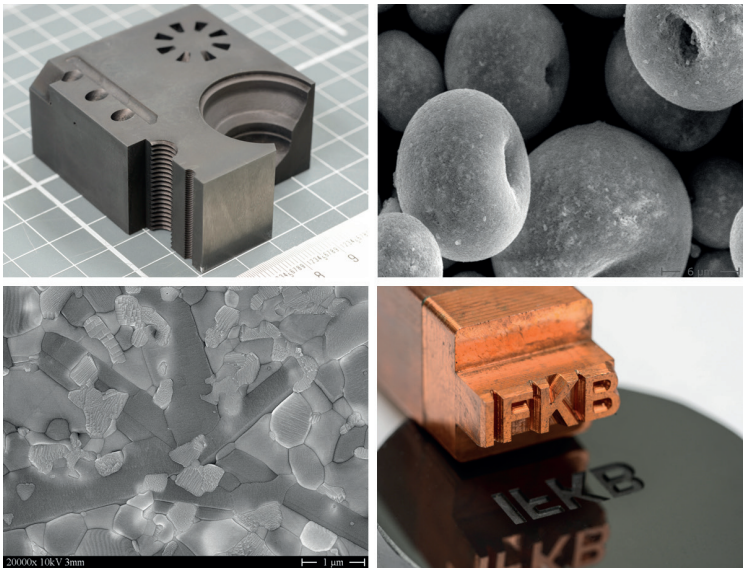
Ulrich Schmitt-Radloff

Werkstoff- und Prozessentwicklung für funkenerosiv bearbeitbare ZTA Keramiken mit NbC- und TiC Dispersion



Universität Stuttgart

Werkstoff- und Prozessentwicklung für funkenerosiv bearbeitbare ZTA Keramiken mit NbC- und TiC Dispersion

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der Universität Stuttgart
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Ulrich Schmitt-Radloff

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Vorwort und Danksagung

Die vorliegende Arbeit ist während meiner Tätigkeit als wissenschaftlicher Mitarbeiter am Institut für Fertigungstechologie keramischer Bauteile (IFKB) der Universität Stuttgart entstanden.

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Stuttgart, im Februar 2018
Ulrich Schmitt-Radloff

Formelzeichen und Abkürzungen

ΔK_C^D	MPa√m	Rissumlenkung durch Druckspannungsfelder
ΔK_C^M	MPa√m	umwandlungsinduzierte Mikrorissigkeit
ΔK_C^T	MPa√m	Umwandlungsverstärkung
A	mm^2	Probenquerschnitt
A	m^2	Scherfläche
Al_2O_3		Aluminiumoxid
ATZ		*alumia toughened zirconia*
b	mm	Breite des Probenkörpers
c	mm	halbe gemittelte Risslänge
c	mm	Risslänge an der Oberfläche
CeO_2		Ceroxid
d	mm	arithmetisch gemittelte Diagonalen des Eindruckes
d	mm	Scheibendurchmesser
d	mm	Mittelwert der Abstände zwischen den Achsen der inneren und äußeren Auflagerollen (Vierpunktbiegeversuch)
d	nm	Netzebenenabstand
E	GPa	E-Modul
F	N	Kraft
F	N	Eindringlast
f	Hz	Frequenz des Schwinkreismodulus
F	N	Höchstkraft bei Probenbruch
F	N	Scherkraft
f_e	Hz	Entladefrequenz
f_p	Hz	Impulsfrequenz
FSZ		*fully stabilized zirconia*
G	GPa	Schubmodul
G*	Pa	komplexer Schubmodul
G`	Pa	Speichermodul
G``	Pa	Verlustmodul
h	mm	Werkstückhöhe
h	mm	Höhe des Probenkörpers

h	m	Plattenabstand
HP		heißgepresst
HV	$kpmm^{-2}$	Härtewertangabe nach Vickers
I	A	Stromstärke
I	A	Arbeitsstrom
i_e	A	Entladestrom
K		Geometriefaktor
$K_{app,0}$	MPa√m	Lastspannungsintensitätsfaktor
K_{I0}	MPa√m	R-Kurven abhängiger Anteil des Spannungsintensitätsfaktors
K_{tot}	MPa√m	globaler Spannungsintensitätsfaktor
l	mm	Abstand der Mittelpunkte der Auflagerollen (Dreipunktbiegeversuch)
l	mm	Abstand der Messspitzen
LVE		linear-viskoelastischer Bereich
m	g	Probenmasse
m		Weibullmodul
$MgAl_2O_4$		Spinell
m_{PL}	g	Masse der Probe an Luft
m_{PW}	g	Masse der Probe in Wasser
n		natürliche Zahl
Nb_2O_5		Diniobpentaoxid (Niob(V)-oxid)
NbC		Niobcarbid
P	N	aufgebrachte Kraft beim Vickerseindruck
$P_e(t)$	W	Entladeleistung
P_f		Versagenswahrscheinlichkeit
PSZ		partially stabilized zirconia
r	mm	Probenradius
R_a	µm	arithmetischer Mittenrauwert (Perthometer)
REM		Rasterelektronenmikroskopie
R_m	Ω	gemessener Messwiderstand
R_z	µm	gemittelte Rautiefe (Perthomether)
S_a	µm	arithmetischer Mittenrauwert (WLI)
SiO_2		Siliziumdioxid (Kieselglas)
SPS		*spark plasma sintering*
S_z	µm	gemittelte Rautiefe (WLI)

t_0	µs	Pausendauer
Ta_2O_5		Ditantalpentaoxid (Tantal(V)-oxid)
t_d	µs	Zündverzögerungszeit
t_e	µs	Entladedauer
t_i	µs	Impulsdauer
TiC		Titancarbid
TZP		*tetragonal zirconia polycristal*
u	mm/min	Vorschubgeschwindigkei
u_e		Entladespannung
$\hat{u}_i$		Leerlaufspannung
v	mm/s	Schergeschwindigkeit
V_m	%	monokliner Phasenanteil
V_t	%	tetragonaler Phasenanteil
W_e	J	Entladeenergie
WLI		Weißlichtinterferrometrie
W_t	µm	Welltiefe (Perthomether)
X_m		monoklinen Intensitätsanteil
Y_2O_3		Yttriumoxid
YAG		Yttrium-Aluminium-Granat
ZrO_2		Zirkonoxid
ZTA		*zirconia touhened alumina*
$\dot{\gamma}$	s^{-1}	Scherrate
Θ	°	Beugungswinkel
κ	S/m	elektrische Leitfähigkeit
λ		Frequenzverhältnis
λ	nm	Wellenlänge der Strahlungsquelle
ν		Querkontraktionszahl
Π	V	Peltierkoeffizient
ρ	Ωm	spezifischer el. Widerstand
ρ_L	g/mm^3	Dichte der Luft
ρ_p	g/mm^3	Probendichte
ρ_W	g/mm^3	Dichte des Wassers
σ	MPa	Bruchspannung
σ	MPa	aufgebrachte Biegespannung

σ_0	MPa	charakteristische Weibullfestigkeit
σ_c	MPa	kritische Bruchspannung
σ_{f3P}	MPa	Biegefestigkeit Dreipunktbiegeversuch
σ_{f4P}	MPa	Biegefestigkeit Vierpunktbiegeversuch
τ		Tastverhältnis
τ	MPa	Schubspannung
ϕ		Entladeverhältnis
χ		Eigenspannungsfaktor
Ψ		Geometriefaktor

Inhaltsverzeichnis

1 Einleitung 1

2 Zielsetzung und Arbeitsplan 3

3 Grundlagen und Stand der Technik 6

3.1 Herstellungstechnik von oxidkeramischen Hochleistungskeramiken 6
3.1.1 Rohstoffgewinnung und Rohstoffaufbereitung 7
3.1.2 Masseaufbereitung und Compounding 8
3.1.3 Formgebung, chemische Technik und Wärmebehandlung 12
3.1.4 Hartbearbeitung 19

3.2 Funkenerosive Hartbearbeitung von Hochleistungskeramiken 21
3.2.1 Grundlagen der funkenerosiven Bearbeitung 22
3.2.2 Funkenerosive Bearbeitung von el. leitfähigen Keramiken 31

3.3 Oxidkeramische Werkstoffsysteme 34
3.3.1 Aluminiumoxid 34
3.3.2 Zirkoniumdioxid 35
3.3.3 Zirkoniumdioxidverstärkte Dispersionskeramiken 39
3.3.4 Plateletversärkte Dispersionskeramiken 40

3.4 Hartstoffphasen und Sinteradditive 43

3.5 Mehrphasige keramische Systeme mit NbC- und TiC Dispersion 47

3.6 Verwendete Charakterisierungsverfahren 52
3.6.1 Mechanische Eigenschaften 52
3.6.2 Bruchzähigkeit 62
3.6.3 Charakterisierung der Compounds 67

4 Experimentelles Vorgehen zur Entwicklung der Dispersionskeramiken 72

4.1 Keramische Ausgangspulver 72

4.2 Herstellung der Heißpresspulver 76
4.2.1 Masseaufbereitung im Labormaßstab 76
4.2.2 Masseaufbereitung für die Sprühgranulation 76

4.3 Formgebung und Sintern der Proben und Halbzeuge 78

4.4 Mechanische und elektrische Charakterisierung der Proben 79

4.5 Funkenerosive Bearbeitung der Proben 80

5 Eigene Untersuchungen zur Entwicklung von NbC- und TiC Dispersionskeramiken 82

5.1 Variation des Stabilisatorgehalts (ZTA – NbC) 82

5.2 Variation des NbC Gehaltes (ZTA - NbC) 88

5.3 *In situ* Verstärkung mit Cerhexaaluminaten (ZTA - NbC) 94

5.4 Einfluss von Sinteradditiven 100

5.4.1 ZTA-TiC (Nb_2O_5 / SiO_2 / $MgAl_2O_4$) 100

5.4.2 ZTA-NbC (Nb_2O_5 / SiO_2 / $MgAl_2O_4$) 106

6 Eigene Untersuchungen zur Prozessentwicklung für NbC- und TiC Dispersionskeramiken 112

6.1 Herstellung von ZTA-NbC Heißpresspulvern im Labormaßstab 112

6.1.1 Variation der anteiligen Mahldauer des NbCs im Masseversatz 112

6.2 Referenzmaterial für die Prozessentwicklung 118

6.2.1 ZTA-TiC 118

6.2.2 ZTA-NbC 118

6.3 Herstellung von ZTA-TiC Heißpresspulvern mittels Sprühgranulation 119

6.3.1 Untersuchungen zur Feinmahltechnik (ZTA-TiC) 119

6.3.2 Untersuchungen zur Sprühtrocknung der Schlicker (ZTA-TiC) 122

6.4 Herstellung von ZTA-NbC Heißpresspulvern mittels Sprühgranulation 137

6.5 Thermische Prozesstechnik zur Konsolidierung der Dispersionskeramiken 145

6.5.1 SPS-Sintern vs. Heißpressen ZTA-TiC 145

6.5.2 SPS-Sintern vs. Heißpressen ZTA-NbC 152

6.5.3 Heißpressen von Keramiken mittels industrieller Presstechnik 160

7 Funkenerosive Bearbeitung der Keramiken 167

7.1 Drahterosion ZTA-NbC - Variation Stabilisatorgehalt 167

7.2 Drahterosion ZTA-NbC - Variation NbC Gehalt 171

7.3 Drahterosion ZTA-NbC - Cerhexaaluminate 176

7.4 Drahterosion von Keramiken mit Sinteradditven 180

7.4.1 ZTA-TiC mit Sinteradditiven 180

7.4.2 ZTA-NbC mit Sinteradditiven 183

7.5 Drahterosion SPS-gesinterter und heißgepresster Keramiken 188

7.5.1 ZTA-TiC 188

7.5.2 ZTA-NbC 191

7.6 Mechanische Eigenschaften nach der Drahterosion 194

7.6.1 Sprühgranulierte und mittels Laborheißpresse gefertigte ZTA-NbC Keramiken 194
7.6.2 Sprühgranulierte und mittels industrieller Presstechnik heißgepresste ZTA-TiC und ZTA-NbC Keramiken 197

8 Diskussion der Ergebnisse 204

8.1 Diskussion der Ergebnisse der Materialentwickung und der funkenerosiven Bearbeitung von NbC- und TiC Dispersionskeramiken 204
8.1.1 Einfluss des Stabilisatorgehaltes auf ZTA-NbC 204
8.1.2 Variation des NbC Gehaltes in ZTA-NbC 207
8.1.3 Einfluss von CA6 Ausscheidungen in ZTA-NbC 210
8.1.4 Einfluss von Sinteradditiven auf ZTA-TiC 212
8.1.5 Einfluss von Sinteradditiven auf ZTA-NbC 213

8.2 Diskussion der Ergebnisse der Masseaufbereitung 215
8.2.1 Einfluss der Mahldauer des Niobcarbids auf die mechanischen Eigenschaften von ZTA-NbC 215
8.2.2 Einfluss des Mahlgrads auf die mechanischen Eigenschaften von ZTA-TiC 217
8.2.3 Sprühgranulation von ZTA-TiC 218
8.2.4 Sprühgranulation von ZTA-NbC 222

8.3 Diskussion der Ergebnisse der thermischen Prozesstechnik 224
8.3.1 SPS-Sintern vs. Heißpressen von ZTA-TiC 224
8.3.2 SPS-Sintern vs. Heißpressen von ZTA-NbC 228
8.3.3 Diskussion der Ergebnisse der mit industrieller Presstechnik hergestellten Keramiken 232

8.4 Diskussion der mechanischen Eigenschaften nach der Drahterosion 233

9 Zusammenfassung und Ausblick 235

10 Literaturverzeichnis 240

Extended Abstract

I. Introduction

High performance structural ceramics show a profile of properties which make them attractive for numerous applications. High hardness combined with high bending strength promise superior product properties. The high hardness of the ceramics is beneficial in terms of wear. However, in case of hard machining these beneficial characteristics lead to low cutting performance and the need to use ultra-hard and expensive diamond grinding media and tools. Classical machining by milling or turning is only applicable to shape green and white bodies. In case of hard machining manufacturing processes grinding, lapping or honing are suitable. Hard machining of ceramics is expensive in general due to the low machining rates and the mandatory use of diamond tools. Electrical discharge machining (EDM) of high performance ceramics can bridge this gap as the EDM process allows the machining of the material independently of its hardness. In the field of hard machining of ceramics customized parts with high shape complexity and narrow tolerances can be economically manufactured by electrical discharge machining. In order to be able to apply EDM technology the workpiece has to be electrically conductive (min. 1 S/m). Since the late 1980s material designers developed ceramics which fulfill this requirement [NKH89]; [GP90]; [MGV11]; [PL04]; [MVP10]; [LKB13a]; [LKB12]; [KLR05]; [KDL88]. ED-machinable ceramics featuring good mechanical properties combined with electrical conductivity can be applied to produce load-bearing machine elements and wear resistant parts. ZTA-TiC ceramics are known for their high bending strength and high hardness [Lan14]; [LKB12]; [LKB13b]; [LKG13]; [GSK17]. However, fracture resistance is still limited. In the past applications in mechanical engineering such as punches, dies or inlays for injection molds suffered from this limited fracture resistance. Defects detected in large size blanks manufactured in industrial hot press equipment according to the previous state-of-the-art hint at an insufficiently elaborated manufacturing process. Peculiarly the lack of suitable processing parameters for the manufacturing of spray dried pressing feedstocks was identified as one of the main reasons for poor material properties. Many of the components ED-machined from these large blanks failed in the application due to insufficient bending strength and fracture resistance. The manufacturing quality of ceramics is directly linked to their failure behavior. Ceramics are typical materials showing brittle failure based on the principle of the weakest link. Thus, at a given - typically low - fracture resistance defect sizes and morphologies determine the strength of ceramics. Strength is limited by the local stress concentration as the result of the largest defect in the load bearing area. Due to the fact that ceramics obtain their final properties after sintering defects often appear subsequently to this final process step. Therefore the classification of sintered parts as reject is an unfortunate drawback. The better part of the value chain is passed and reject costs are high. Consequently, strategies to improve process quality and a closer focus on processing technologies are required to avoid or minimize defects. From a manufacturing point of view this is equally important as the classical material development itself. Only a holistic development approach by combining material engineering and process engineering can lead to enhanced properties of ceramic components with superior performance in the desired target applications. Due to the concatenation of processing steps typical for the manufacturing of

ceramics, the development of ceramic components and their implementation can only be carried out considering a thorough elaboration of materials and industrial manufacturing processes.

II. Objectives

The topic of the present thesis is a comprehensive approach by combining material and process development of zirconia toughened alumina (ZTA) based electrical discharge machinable ceramics. This includes material engineering aspects and aspects that are part of the subsequent processing steps. The latter implies compounding including milling technology, spray drying as well as thermal processing of the manufactured powders. The all-embracing aim is the development of suitable processing parameters for the manufacturing of electrical discharge machinable ceramics consolidated by hot pressing and spark plasma sintering. This includes the manufacturing of flowable granulates by spray drying and adjusted upstream processing steps such as dispersing and milling of ceramic dispersions.

The material engineering focuses on the field of ZTA which is reinforced by niobium carbide (NbC) to enable the electrical discharge machining of the material. NbC compared to titanium carbide (TiC) appears to be a more suitable candidate due to its higher intrinsic toughness and commercial availability in smaller grain sizes. Thereby ZTA-NbC promises improved mechanical properties such as higher bending strength, high hardness and enhanced toughness compared to ZTA-TiC. Literature gives some references on TZP-NbC [FLK99]; [NKH89]; [Nip17]; [PHF02]; [SMC08] and Al_2O_3-NbC [AC06]; [ACS05]; [ACC12]; [AGM01]; [AGM00]; [ASG03]; [AFG17a]; [AFG17b]; [PTB03]; [PTB02]; [PBB98]. The ZTA-NbC material system is not yet explored. Figure 1 outlines the work plan and the assumed influences on the material properties.

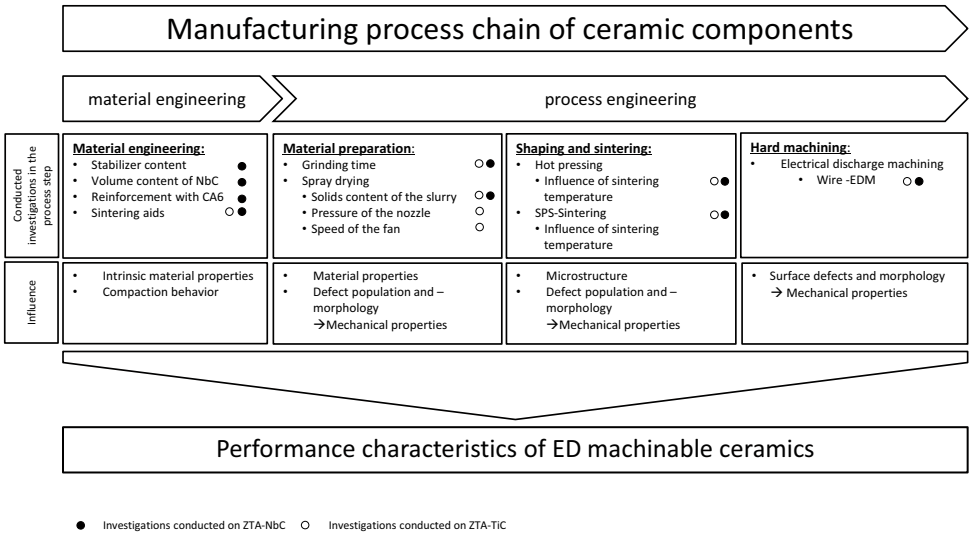

Figure 1: Work plan of the thesis and the classification of the investigations in the process and development chain

A refinement of the ZTA-NbC recipes with respect to stabilizer content of the zirconia dispersion, the volume content of the el. conductive phase, reinforcement of the ceramics by *in situ* formation of ceria hexaaluminates and the influence of sintering aids such as SiO_2, Spinel and Nb_2O_5 is pursued in the materials development section to achieve superior properties of the ceramics. Since ED-machinability is essential, all newly developed materials were investigated by wire electrical discharge machining to obtain information on surface quality, surface layers affected by the EDM process and the process stability. Machining parameters were kept constant to allow a comparison of the results. It is known that machining of brittle materials may lead to serious surface damage that subsequently results in impeded mechanical properties such as bending strength and reliability. Detailed studies on the reliability and the bending strength in the ED-machined state were executed for selected material compositions in order to investigate and quantify the influence of the electrical discharge machining of ZTA-NbC on the mechanical properties.

III. Experimental Results

Stabilizer Content of ZTA-NbC

The influence of the yttria stabilizer content of the zirconia dispersion on the mechanical properties of ZTA-NbC was studied by adjusting the stabilizer contents in 0.25 mol-% increments in the range of 0.75 - 2 mol-% Y_2O_3. The investigated ceramic had a phase composition of 24 vol.-% NbC, 17 vol.-% ZrO_2 and 59 vol.-% Al_2O_3. The results show, that best mechanical properties with respect to 4-point bending strength and toughness were achieved at low stabilizer contents (≤ 1.25 mol-%). Highest bending strength was observed at a stabilizer content of 1.25 mol-% (774 ± 82 MPa), while best fracture toughness - according to the ISB method - was observed at 1 mol-% yttria (4.95 MPa√m). As the content of conductive phase was constant electrical conductivity is not much influenced by the variation of stabilizer content, while Vickers hardness strongly improves at rising stabilizer content to 1.5 mol-% and then levels off (> 1800 HV10) (figure 2).

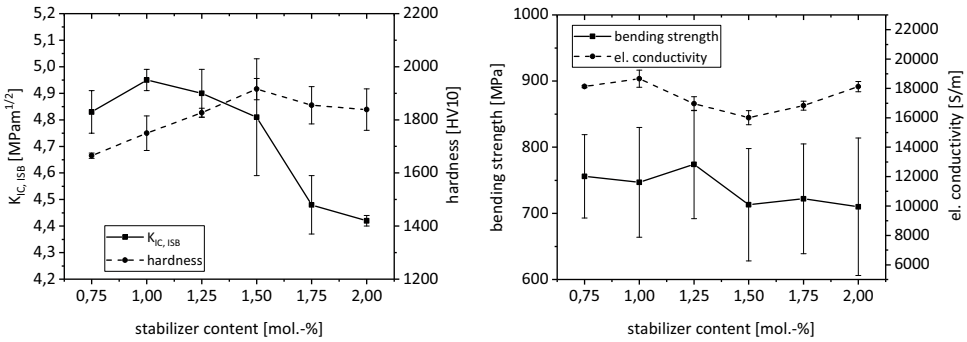

Figure 2: Left: fracture toughness $K_{IC,ISB}$ and Vickers hardness vs. stabilizer content; right: bending strength and el. conductivity vs. stabilizer content [SKG17a]

Electrical discharge machining by wire cutting was possible for all material compositions, but the machining was accompanied by several wire breaks which appeared regardless of the present stabilizer content. Apparently, rising stabilizer content causes a change in the material removal mechanism. High stabilizer contents favor the melting and vaporization of the zirconia phase and cause rougher surface qualities.

NbC content of ZTA-NbC

Investigations on the influence of NbC content on the mechanical properties and the machinability by wire electrical discharge machining show that low volume contents of NbC (≤ 28 vol.-%) are beneficial for high bending strength, but detrimental to ED-machining. ED machining is accompanied by frequent wire breaks: process stability is insufficient which presents an economic drawback. Stable machining conditions can be achieved by increasing the content of the conductive NbC dispersion in the ZTA matrix to > 28 vol.-%. Variation of the NbC phase content strongly influences el. conductivity. However, increasing the NbC content constrains densification during sintering. As under the chosen sintering conditions full density at high NbC contents cannot be achieved, hardness and stiffness of the materials decrease. The influence of impeded densification counteracts the desired effect of rising NbC content, for which - as a consequence of the rule of mixture – higher hardness and Young's modulus would be expected. The surface quality of the ED machined samples shows essential improvements with rising stabilizer content. With rising NbC content the improvement of the electrical and thermal conductivity leads obviously to a reduced tendency to vaporize Al_2O_3. Thereby smoother surfaces are obtained by formation of a pronounced glassy layer. The surface gets smoothened and gassy inclusions in the influenced layer decrease with rising NbC content.

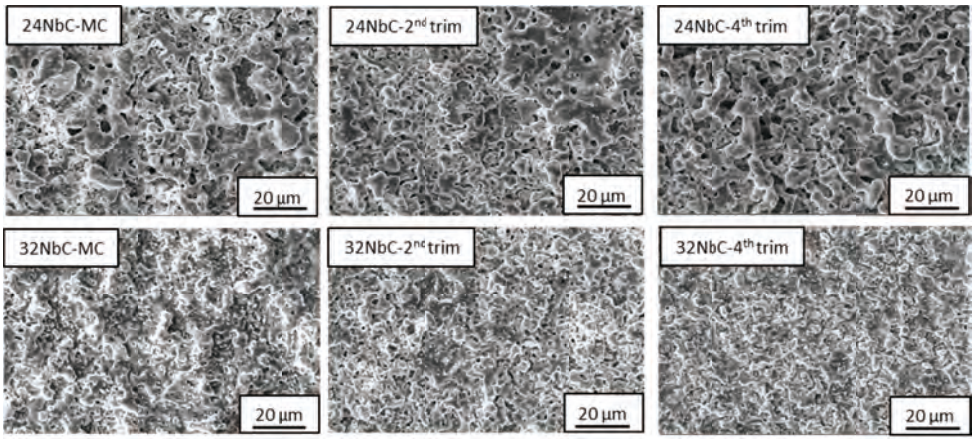

Figure 3: Electrical discharge machined surfaces of 24 vol.-% NbC (top) and 32 vol.-% NbC containing ZTA-NbC (left: main cut; middle: 2nd trim; right: 4th trim)

CA6 reinforcement of ZTA-NbC

The reinforcement of ZTA-NbC with *in situ* formed cerium hexaaluminate platelets (CA6) was successfully accomplished.
Mechanical properties such as bending strength and fracture toughness can be strongly improved under selected conditions. Especially the fracture toughness of the material benefits from the *in situ* reinforcement. While bending strength shows best properties (844 ± 88 MPa) for low CA6 contents (2.5 vol.-%), fracture toughness rises continuously with increasing volume content of CA6 and reaches its maximum at CA6 contents of 7.5 and 10 vol.-% (~ 5.3 MPa√m). Contrary to former investigations on ZTA-TiC-CA6 [Lan14] the el. conductivity is improved by the *in situ* reinforcement with CA6.
The ED machining of all material compositions by wire cutting was possible. The lower melting point of CA6 platelets [MBC75] causes improved cutting performances for the main cut and the first two trimming operations. The surface quality of low alloyed ZTA-NbC-CA6 ceramics (≤ 5 vol.-% CA6 platelets) is improved by lowering the melting temperature of CA6 compared to plain alumina.

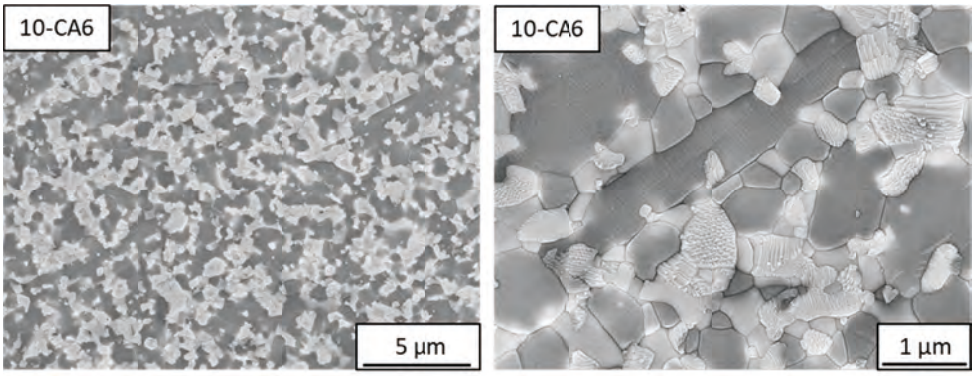

Figure 4: Microstructure of ZTA-NbC containing 10 vol.-% CA6 platelets

Influence of sintering aids on material properties and sintering behavior of ZTA-NbC and ZTA-TiC

Sintering aids as Spinel, Nb_2O_5 and SiO_2 can help to improve the compaction and sintering behavior of ZTA-NbC and ZTA-TiC. This is even more pronounced in case of the fine grained ZTA-NbC. Even though the densification of those composite ceramics is enhanced by the addition of these sintering aids and the defect size and defect population decreases, but the mechanical properties of the undoped composites are still better. However, the addition of sintering aids is more beneficial when the production is scaled up to manufacture large size blanks that suffer most from sluggish compaction behavior. In case of ZTA-TiC the addition of sintering aids leads to thicker surface layers by the ED machining. The ZTA-NbC doping with sintering aids has little influence on machining behavior, different material compositions show only marginal variations in machining performance and quality.

Influence of grinding technology and residence time on the mechanical properties

For ZTA-NbC, as well as for ZTA-TiC, an analysis of the milling process was carried out. The influence of residence time in the mill and the resulting particle size distributions on the mechanical properties were studied for ZTA-NbC attrition milling and for ZTA-TiC bead milling. The investigations show, that an extended residence time of the NbC in the slurry leads to homogenously dispersed ceramics and to a refinement of the NbC phase. Particle size of ZrO_2 and Al_2O_3 is not much influenced by the earlier addition of NbC to the slurry. Due to the homogenization of the ceramic, combined with improved deagglomeration of NbC, mechanical properties such as bending strength (693 – 766 MPa) and fracture toughness ($K_{IC,ISB,30min}$ = 4,82 ± 0,2 MPa√m); $K_{IC,ISB,120min}$ = 4,89 ± 0,085 MPa√m) can be improved. Surprisingly, the el. conductivity of ZTA-NbC decreases with rising residence time of NbC in the slurry. This can be explained by the change of the grain morphology of NbC. At low residence time NbC grains consist of agglomerated smaller crystallites and the aggregates have an elongated shape. Due to the deagglomeration of NbC these elongated aggregates are separated into individual grains. The shape effect seems to offset the size effect. As elongated particles already form a percolating conductive network at much lower volume contents the deagglomeration leads to a reduction of conductivity which is not fully compensated by the larger number and smaller size of NbC particles.

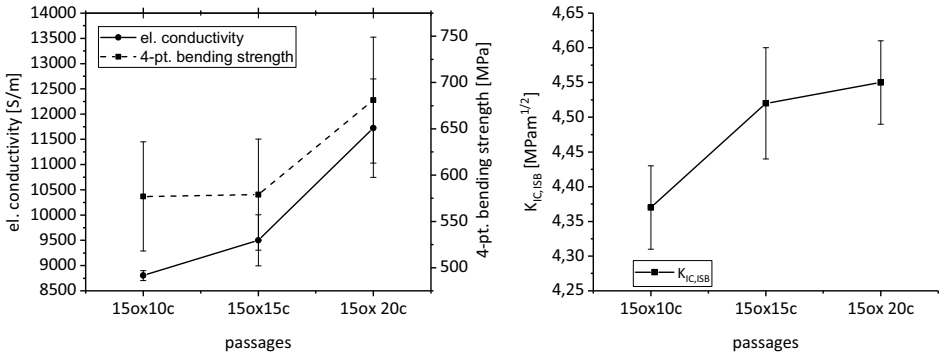

Figure 5: El. conductivity (left), bending strength (left) and fracture toughness (right) of ZTA-TiC compounds with different residence time in the mill

For the processing of ZTA-TiC by spray drying the ceramic slurry has to be milled. This is necessary for good homogenization and deagglomeration of all the constituents. Due to the change in milling technology, from attrition milling to bead milling, investigations on the processing are required. Possible setups are milling the dispersions passways (pass the slurry through the mill and then mill the resulting product again) and by recirculating the dispersion over the mill from a stirred storage container. The results show, that milling passways by ensuring a plug flow is more suitable than recirculating for the preparation of larger batches of suspension. With increasing number of passages grain size gets reduced and homogeneity increases. At the same time size distribution stays narrow. These dispersion properties

lead to improved values for bending strength and fracture toughness in the sintered materials (Figure 5). The refinement of the microstructure causes an increase of el. conductivity which is the most important factor for the electrical discharge machinability (Figure 5). Best properties were achieved by milling the oxide phases 15 times and a subsequent milling of the suspension containing the TiC for 20 passages.

Spray drying of ZTA-TiC

Investigations on spray drying the ZTA-TiC slurries included experiments on the main influence factors such as solid content, temperature, fan speed and atomization pressure at the two component jet nozzle. It was observed that best mechanical properties of the hot pressed ceramics were achieved by using a wider particle size distribution of the spray dried intermediates. Contrary to the use of spray dried intermediates for uniaxial pressing a narrow particle size distribution does not cause best mechanical properties. High solid contents of the slurry cause a higher viscosity of the slurry and thereby higher average particle sizes. The spray dried granules show a nearly spherical morphology with apple cheeks on one side. The existence of satellites on the surface of bigger granules can be effectively suppressed by using higher solid contents and spray drying temperatures. The variation of fan speed and pressure of the nozzle can help to produce intermediates of high quality with superior properties for the hot pressing process. If parameters were set to produce intermediates with wide particle size distributions and nearly spherical morphology the hot pressed ceramics show mechanical properties equivalently or improved compared to hot pressed ceramics starting from attrition milled, dried and sieved powders. Due to the use of spray dried intermediates the mold filling behavior can be improved, larger blanks can be pressed in molds of given size and defects can be avoided.

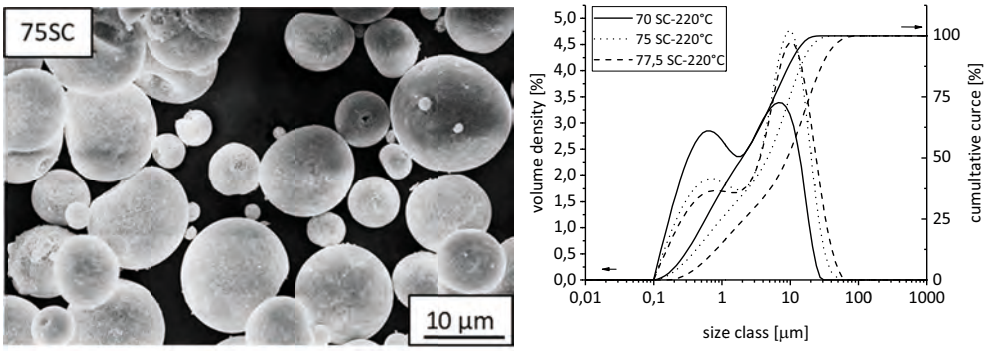

Figure 6: Left: granules of ZTA-TiC slurry containing 75 vol.-% solid content; right Particle size distribution of spray dried intermediates processed out of slurries containing 70, 75 and 77,5 wt.-% solid content

Spray drying of ZTA-NbC

In case of the spray drying of ZTA-NbC the results of the investigations on ZTA-TiC were adapted and only a variation of the solid content was carried out. The ZTA-NbC granulates show a similar dependence of the morphology on the solid content as the ZTA-TiC intermediates studied previously. Again, low solid contents of 70 wt.-% cause a wider particle size distribution and thereby improved mechanical properties such as bending strength and fracture toughness. Still, compared to ZTA-TiC, ZTA-NbC granulates show a much more inhomogeneous distribution of the three phases over the granule diameter. This inhomogeneity can be reduced by rising solid content of the slurries. Spray dried ZTA-NbC intermediates lead to bending strengths comparable to ceramics made from lab-scale prepared powders. Additionally, a slightly improved fracture resistance is provided.

Investigations on HP vs. SPS sintering of ZTA-TiC

In order to investigate the influence of sintering temperature and sintering technique, ZTA-TiC blanks were manufactured by hot pressing and spark plasma sintering in a wide range of sintering temperatures (1450 – 1700 °C). SPS sintered blanks need higher sintering temperatures for full densification (1500 °C) while hot pressed samples show high densities over the whole temperature range. Both sintering techniques lead to blanks that are suitable for applications where high strength and hardness is required. While mechanical properties of hot pressed ZTA-TiC are more insensitive to changes in sintering temperature, SPS sintered samples show a contrary trend.

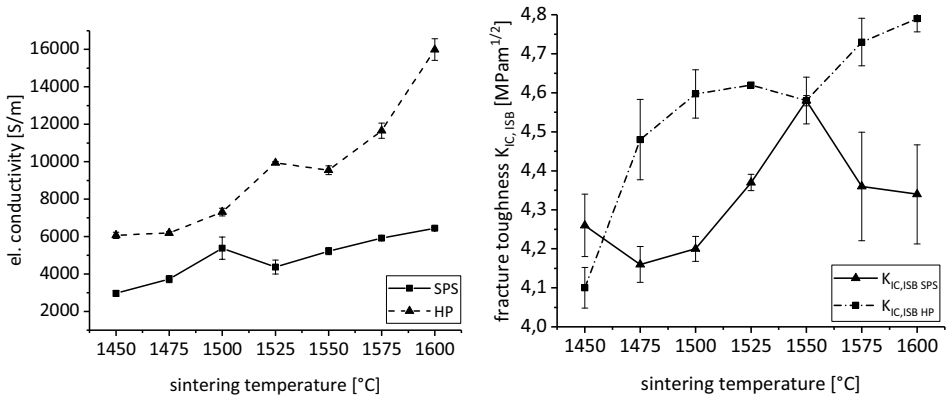

Figure 7: Left: el. conductivity of hot pressed (HP) and spark plasma sintered ZTA-TiC; right: fracture toughness of HP and SPSed ZTA-TiC [SKG18a]

Over the temperature range of 1475 – 1575 °C hot pressed samples show a strength of > 700 MPa and fracture toughness of > 4.5 MPa√m, while SPSed samples show comparable bending strength over a broad sintering range. However, high fracture resistance is only obtained at a sintering temperature of 1550 °C. SPSed materials always show finer grained microstructure and no tendency towards abnormal

grain growth with rising sintering temperature. Hot pressed samples show a much more pronounced tendency for grain growth and TiC grains tend to merge and change their morphology with rising sintering temperature. As a result the el. conductivity in hot pressed material rises stronger with increasing sintering temperature than in SPSed ZTA-TiC. First investigations on selected HP and SPSed samples show that ED machining of SPSed ZTA-TiC is possible. But SPSed materials show inferior surface qualities with respect to average surface roughness and roughness depth. In case of SPSed material subsequent trimming operations do not improve the surface quality while the surface quality of hot pressed materials improves distinctly. Cutting performance of the wire cutting process was lower for the SPSed samples. Obviously the TiC backbone in case of hot pressed samples enhances the electrical and thermal conductivity which in consequence leads to better surface qualities and higher cutting performance.

Investigations on HP vs. SPS sintering of ZTA-NbC

Comparative studies on sintering temperature (1450°C – 1600 °C) for hot pressed and SPSed ZTA-NbC show that HP materials are much less vulnerable to changes in the processing conditions than SPSed materials. In case of HP ZTA-NbC high bending strength of > 700 MPa and hardness (~ 1900 HV10) was achieved over the whole sintering temperature range. Fracture toughness is the most affected mechanical property, toughness rises with rising sintering temperature. The SPSed composites showed much higher parametric sensitivity resulting in a high bending strength only for the sintering temperature of 1575 °C, hardness and fracture resistance are always on a lower level compared to HP ZTA-NbC. Fracture resistance shows a rising trend towards increasing sintering temperature for both sintering techniques. El. conductivity is the only property which is evidently enhanced by changing from HP to SPS. If full densification is achieved the el. conductivity of SPSed material exceeds the HP material by ~ 10,000 S/m.

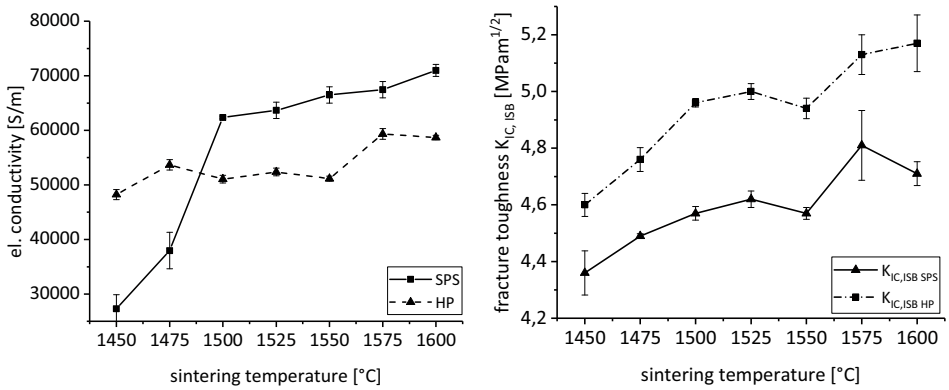

Figure 8: Left: el. conductivity of hot pressed (HP) and spark plasma sintered ZTA-NbC; right: fracture toughness of HP and SPSed ZTA-NbC [SKG28b]

SPSed materials show a refinement of the grain size compared to HP materials manufactured at the same sintering temperature. The most interesting observation is that in case of SPSed ZTA-NbC NbC grains tend to merge and build a percolating scaffold with rising sintering temperature which helps to improve the el. conductivity. Wire electrical discharge machining investigations of ZTA-NbC show that despite the higher conductivity the surface quality of SPSed ZTA-NbC cannot match HP. Cutting performance is slightly improved.

Hot pressing of ZTA-TiC and ZTA-NbC on industrial plant hot presses

Hot pressed blanks with large dimensions (Ø 100 mm, h = 40 mm) of ZTA-NbC and ZTA-TiC show the difficult stabilization of the metastable tetragonal zirconia phase at room temperature by using industrial plants. The samples show an increased content of monoclinic zirconia fraction (ZTA-TiC: 14.8 %; ZTA-NbC: 55.6 %) compared to samples manufactured at laboratory conditions. This increase of monoclinic fraction results in reduced bending strength, fracture toughness and stiffness. Evidently, fast cooling - the prerequisite to retain the metastable tetragonal phase at room temperature – is not possible due to the larger dies and higher volume/surface ratio of blanks manufactured at an industrial scale. This phase transformation is even more pronounced in case of ZTA-NbC due to its lower stabilizer content. The experiments also show, that by the use of spray dried intermediates, the filling of the die is strongly improved and in consequence nearly defect free blanks can be manufactured. The manufacturing of ceramic blanks by industrial plants improves the homogeneity of the ceramic and supports the reliability of the material. Comparative measurements on the Weibull modulus of samples made by laboratory plants and industrial plants show benefits in terms of the reliability of blanks made by industrial plants.

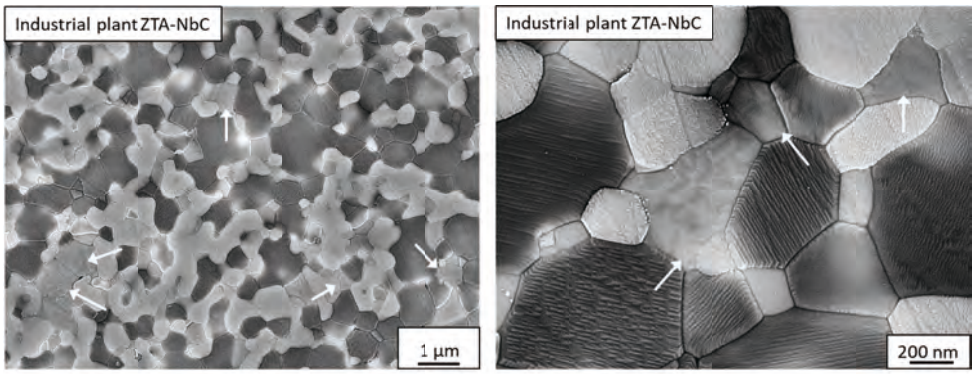

Figure 9: Monoclinic zirconia grains in ZTA-NbC manufactured on industrial plant hot press

Influence of ED machining on the mechanical properties of ZTA-NbC

It was expected that electrical discharge machining of ZTA-NbC influences the mechanical properties i.e. bending strength and reliability due to the formation of a process zone at the machined surface. Investigations on samples cut out of the industrial plant blank show a decreasing trend of bending strength up to the 2nd trimming operation. Further trimming operations cause a subsequent recovery. Contrary to bending strength, the Weibull modulus of the machined samples continuously increases with rising number of trimming operations.

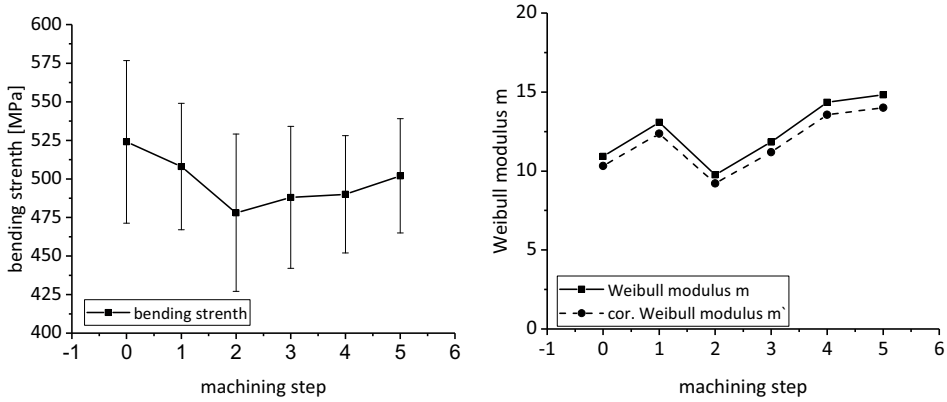

Figure 10: Bending strength (left) and Weibull modulus (right) depending on the machine state (0 = polished; 1 = main cut; 2 = 1st trim; 3 = 2nd trim; 4 = 3rd trim; 5 = 4th trim) [SKG18c]

Further experiments on hot pressed samples made by laboratory plants show a similar behavior. Again, a slightly decreasing trend of bending strength up to the 2nd trimming operation is observed. Further trimming operations result in bending strengths that are on the same level or even higher as the polished ceramics. The Weibull modulus is increased due to the electrical discharge machining operation. The experiments show that electrical discharge machining of ZTA-NbC reduces the bending strength only slightly and helps to improve the reliability of the material. The material is harmed to a little extent by ED machining, the surface near defects present in as fired state are removed and replaced by new defects with an apparently more homogenous defect size and morphology. This fact improves the Weibull modulus and thereby the reliability of the material.

IV. Summary and conclusion

In the present thesis the material system ZTA-NbC was investigated for the first time with respect to its mechanical properties and its suitability for electrical discharge machining. Fundamental compositional parameters affecting the mechanical properties such as stabilizer content, volume content of the

electrically conductive Phase NbC and the reinforcement by *in situ* ceria hexaaluminates were investigated and their influence on the machining process was carved out.

The present work puts the material engineering in the context of a holistic approach, which combines elements of material engineering and process engineering. Therefore the manufacturing process of ZTA-TiC and ZTA-NbC was customized in order to provide performing ceramic intermediates. Suitable parameters for spray drying of ZTA-TiC were developed and subsequently transferred to the material system ZTA-NbC. The influence of compounding techniques including wet milling and the variation of the spray drying parameters on the quality of ceramic intermediates and the mechanical properties of the hot pressed ceramics were systematically investigated. Additionally, the influence of sintering temperature on the microstructural and mechanical properties of ZTA-TiC and ZTA-NbC was investigated for hot pressing and SPS sintering in a comparative study. The study of the influence of sintering temperature and the chosen sintering technology (hot pressing or SPS) helps to adjust the sintering parameters in future studies. It was demonstrated, that SPS sintering may be a suitable shaping and sintering technology for the manufacturing of electrical discharge machinable ZTA based ceramics. A more economic manufacturing of those ceramics could be achieved in future by the shorter dwell and the improved cooling rates of SPS sintering.

However, the study shows that the elaboration of processing conditions in SPS sintering has to be carried out with greater care than in case of the established and very forgiving hot pressing technology. It could be documented that spray dried intermediates help to manufacture ceramic blanks with superior material properties by hot pressing or spark plasma sintering compared to the blanks from laboratory experiments. The performed experiments on ZTA-NbC suggest that this newly developed material system is a suitable candidate as electrical discharge machinable ceramic. The material characteristics of ZTA-NbC include high hardness, high bending strength and attractive fracture toughness and may lay the foundation for customized ceramic components in mechanical engineering. Spray dried intermediates improve the filling properties of the dies and ultimately help to produce large blanks with superior microstructural properties, reduced defect sizes and enhanced reliability.