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Polysiloxane Derived Si(Al)OC Bulk Ceramics for High-Temperature Resisting Sensors

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- Project description
- Ceramic precursor
- Filler route: phase development for MK derived Si-O-C ceramics in the presence of Al, Al_2O_3 fillers
- Summary
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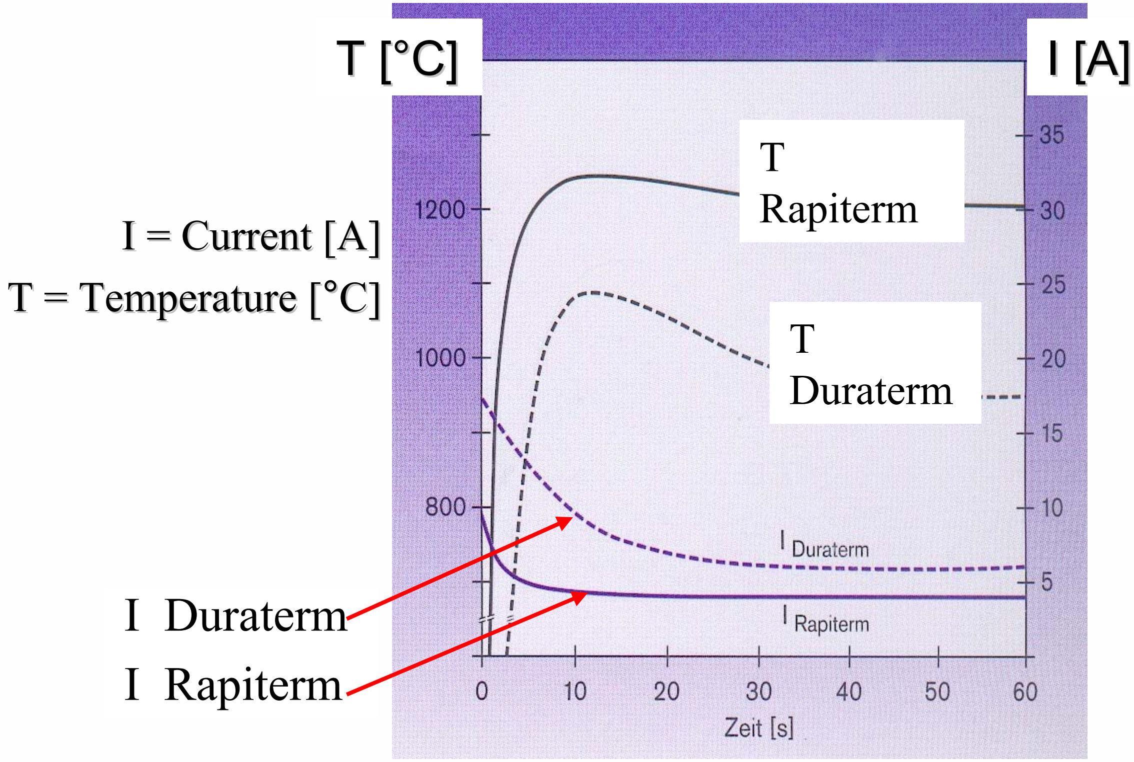
SiOC based ceramic glow plug for diesel engine

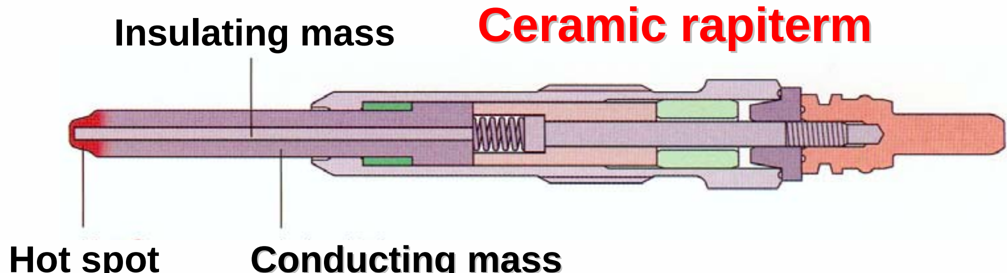
First industrial application of polymer-derived ceramics made from polysiloxanes and a variety of filler materials

- Immediate ignition, even at -20°C
- Reduced emissions
- Durability, lifetime

- Fast heating
- Low current input
- High operation temperature



Ceramic rapiterm



Source: Robert Bosch GmbH

Objectives

Better efficiency factor of the diesel engine ↔ Better management of the burning process in the engine

A ceramic glow plug with temperature and pressure sensors

↓

Design of multifunctional ceramic components having sensoric properties stable at high temperatures based on polysiloxanes and nanoscaled fillers

To increase the thermal stability of the SiOC matrix from the current 1200°C to 1300°C for continuous operation → Incorporation of Al

Filler route

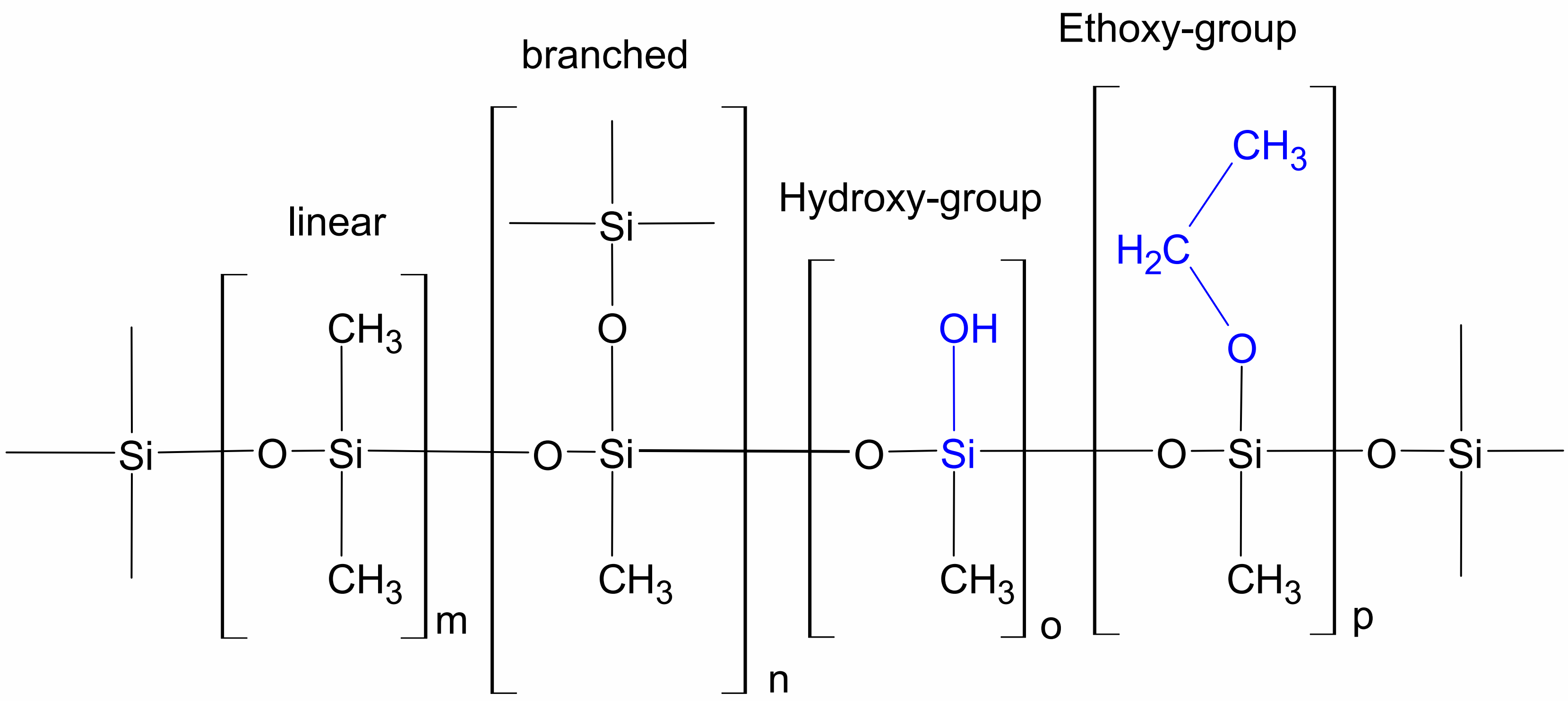
Use of commercially available nanoscaled fillers : Al and Al_2O_3

Ceramic Precursor

Use of commercially available polysiloxanes

- Inexpensive
- Can be processed in air
- Environment friendly

Starting material: polysiloxane Wacker Belsil MK®



Why insertion of Al in polysiloxanes?

Si(Al)OC Ceramics

- **Higher Temperature Resistance**
- **Higher Oxidation Resistance**

Role of Aluminium?

Lower carbon content (Influence on the pyrolysis behavior)
Lower viscosity compared to SiOC
Amorphous up to 1300 °C
No cristobalite formation
Formation of mullite at T > 1400 °C

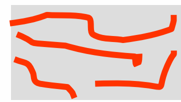
What are the mullite advantages?

- Low thermal expansion coefficient (high thermal shock resistance)
- Low thermal conductivity
- Low electric conductivity and low dielectric constant
- Remarkable creep resistance and good mechanical strength

R. Harshe et al., J. Europ. Ceram. Soc. **24** (2004) 3471
R. Harshe, PhD Thesis, TU Darmstadt (2004); see: http://elib.tu-darmstadt.de/diss/000512/

Filler Route

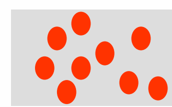
Polymeric Precursor → **MK-Polymer**



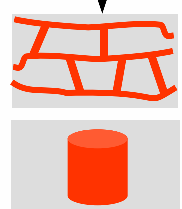
Precursor Modifier → **MK + 1 wt.-% $Zr(acac)_4$ (CLA)**

Powder Preparation → **MK-Polymer+1wt%CLA Al_2O_3 or Al**

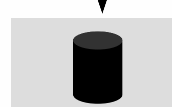
Milling/Sieving (<100 µm)



Forming and Crosslinking → **Warm Press**



Pyrolysis → **1300°C/3h holding time**



CLA = Cross-Linking-Agent

Filler Route

Pyrolysis parameter

Temperatur (°C)	Heating Rate (K/h)	Holding Time (h)
200	50	0
800	25	0
1300	50	3
25	Oven Off	

Ar atmosphere

Post pyrolysis heat treatment parameter

Temperatur (°C)	Heating Rate (K/h)	Holding Time (h)
1300	600	0
1500	300	3
100	600	0
25	Oven Off	

Ar atmosphere

Insertion of Al_2O_3 in MK Polymer

Polymer (MK + CLA)	☎-Al_2O_3 §
37.3 [wt%]	62.7 [wt%]
42 [wt%]	58 [wt%]
100µm	15nm

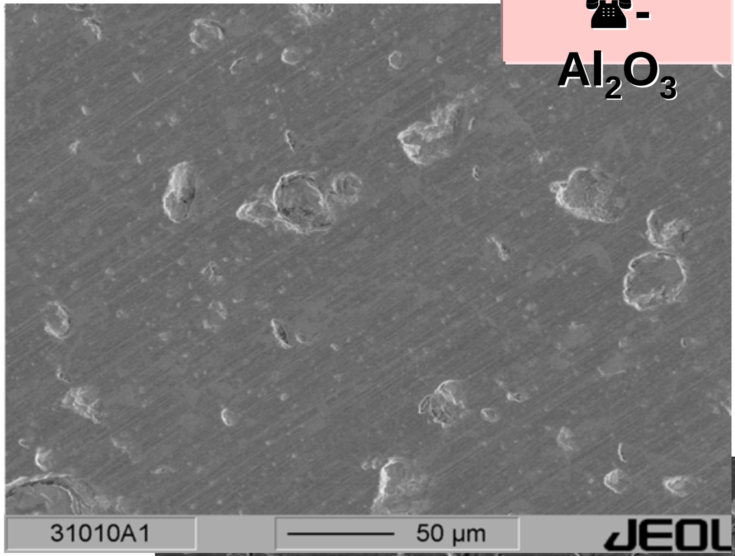
§ Aeroxide AluC Degussa

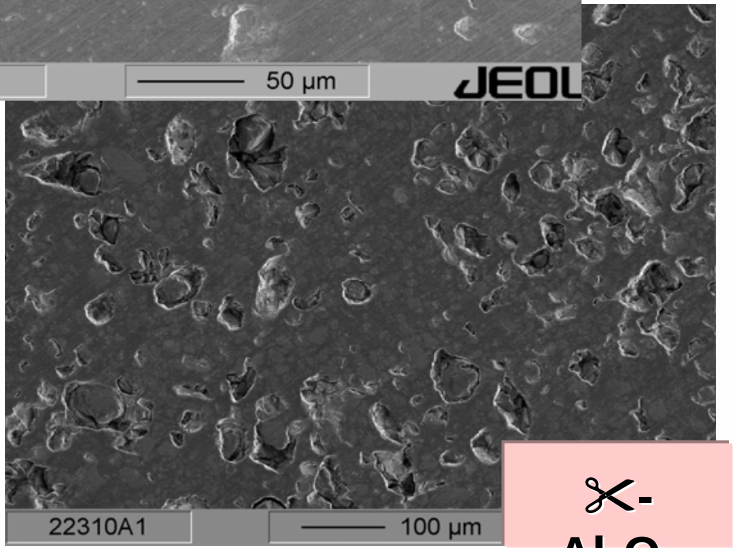
Polymer (MK + CLA)	✂-Al_2O_3 #
37.3 [wt%]	62.7 [wt%]
100µm	150nm

Taimicron TM-DAR

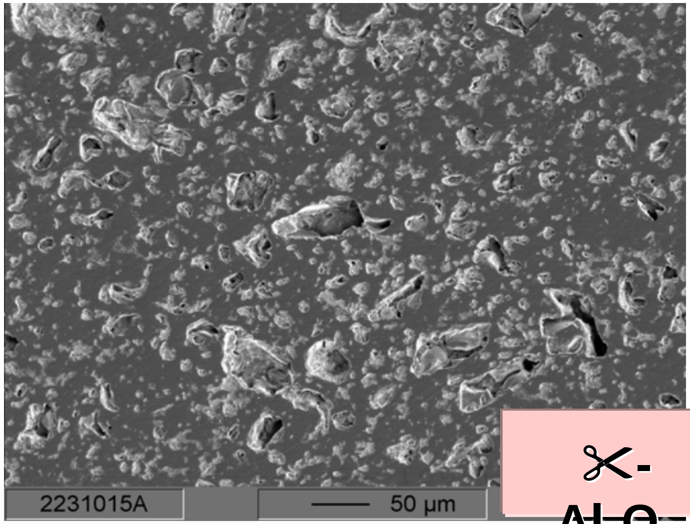
Polymer (MK + CLA) +	Mullite	☎-Al_2O_3	Corundum	Temperature
62.7 [wt%] ☎-Al_2O_3	✞	✞		1300
58 [wt%] ☎-Al_2O_3	✞	✞		1300
62.7 [wt%] ✂-Al_2O_3			✞	1300
	✞		✞	1500

☎-Al_2O_3





✂-Al_2O_3



✂-Al_2O_3

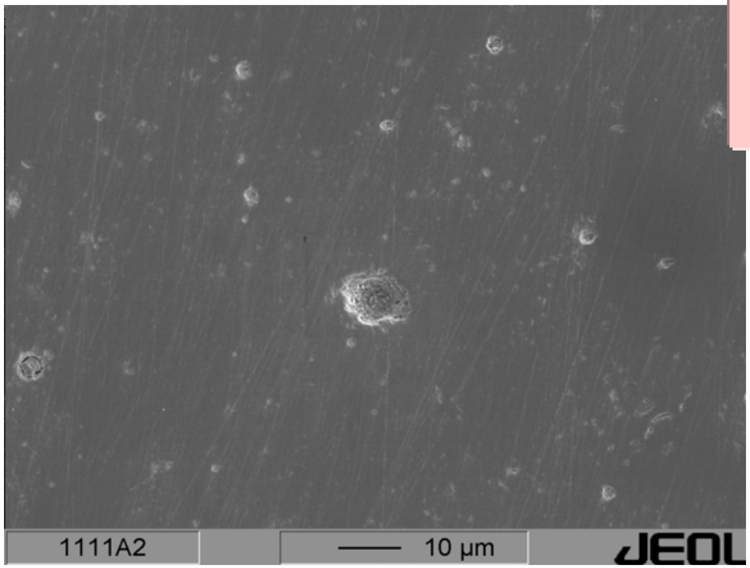
1300°C

1500°C

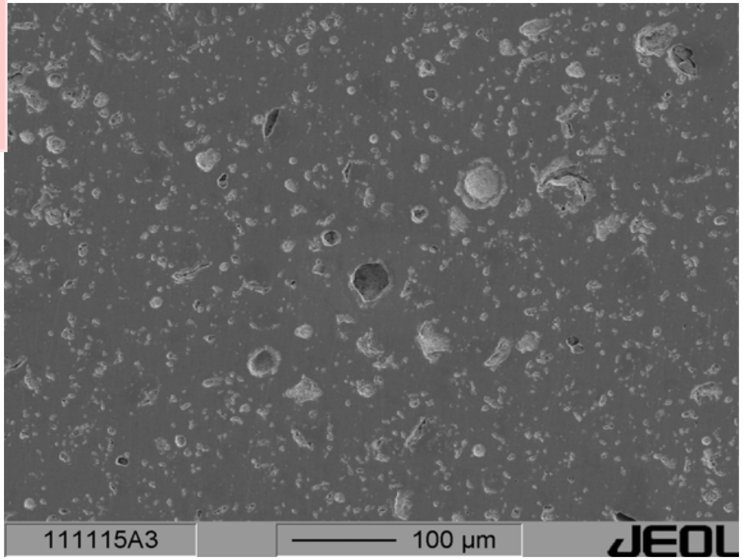
Insertion of Al in MK Polymer

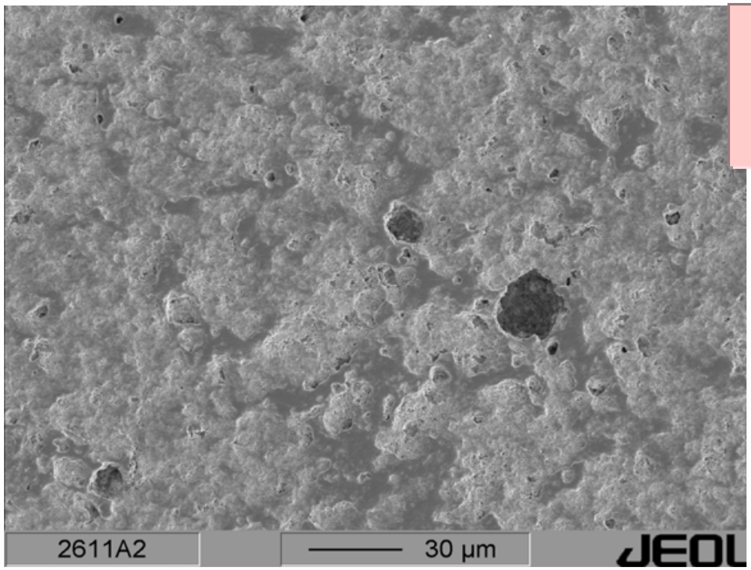
Polymer (MK + CLA)	Al
81.10 [wt%]	18.90 [wt%]
76.93 [wt%]	23.07 [wt%]
71.43 [wt%]	28.57 [wt%]
100µm	50nm

Polymer (MK + CLA) +	Mullite	β-SiC	Corundum	☎- Al_2O_3	Temperature
18.90 [wt%]		✞	✞	✞	1300
	✞	✞	✞		1500
23.07 [wt%]	✞	✞	✞	✞	1300
	✞	✞	✞		1500
28.57 [wt%]		✞	✞	✞	1300
		✞	✞		1500

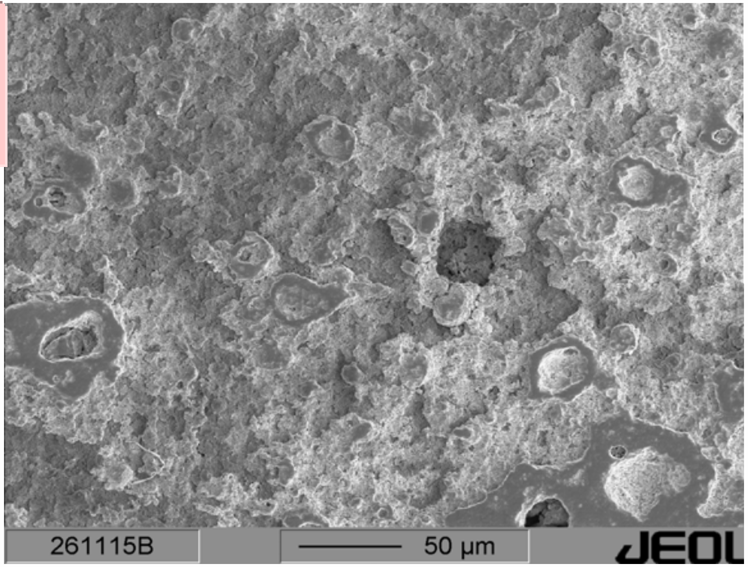


18.90 [wt%]





28.57 [wt%]



1300°C

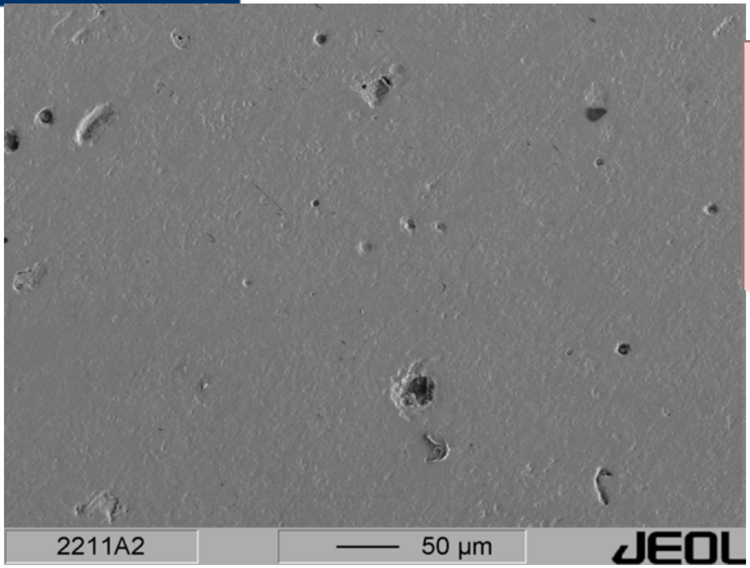
1500°C

Insertion of Al and Al_2O_3 in MK Polymer

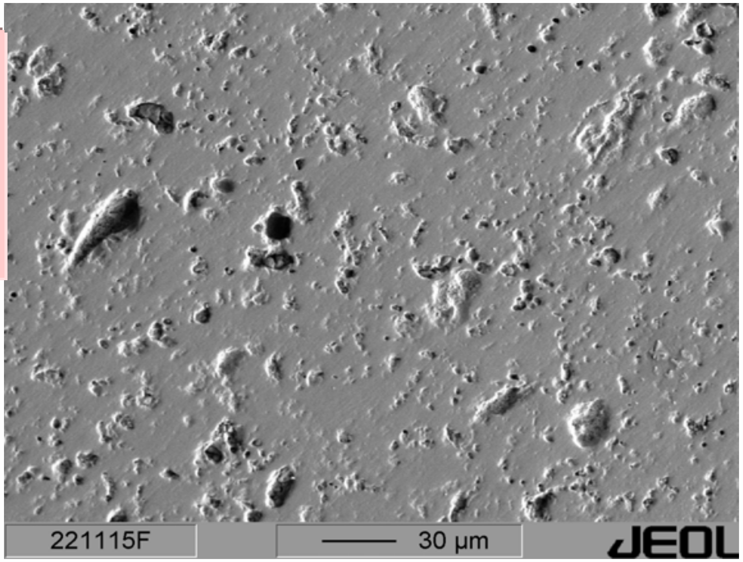
Polymer (MK + CLA)	Al	☎- Al_2O_3§
68.2 [wt%]	9.1 [wt%]	22.7 [wt%]
69.8 [wt%]	11.6 [wt%]	18.6 [wt%]
71.5 [wt%]	16.6 [wt%]	11.9 [wt%]
100µm	50nm	15nm

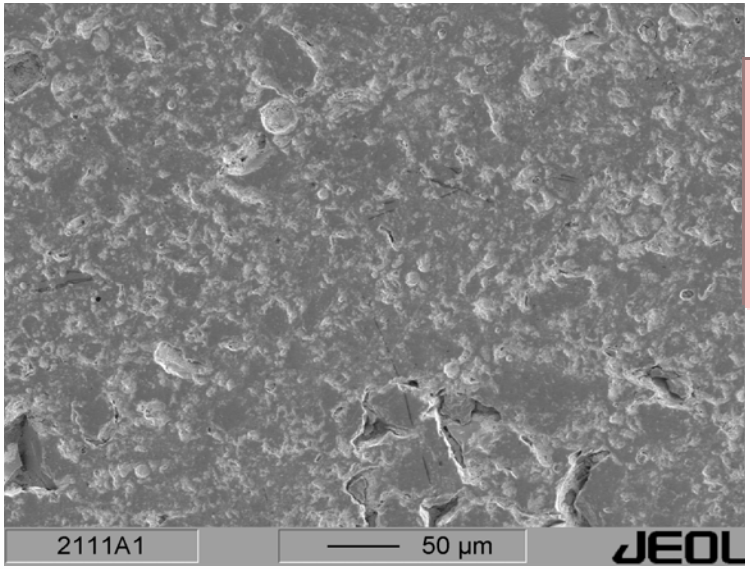
§ Aeroxide AluC Degussa

Polymer (MK + CLA) +	Mullite	β-SiC	Corundum	☎- Al_2O_3	Temperature
9.1 [wt%] Al + 22.7 [wt%] Al_2O_3		✞	✞	✞	1300
	✞	✞	✞		1500
11.6 [wt%] Al + 18.6 [wt%] Al_2O_3		✞		✞	1300
	✞	✞	✞		1500
16.6 [wt%] Al + 11.9 [wt%] Al_2O_3		✞	✞		1300
	✞	✞	✞		1500

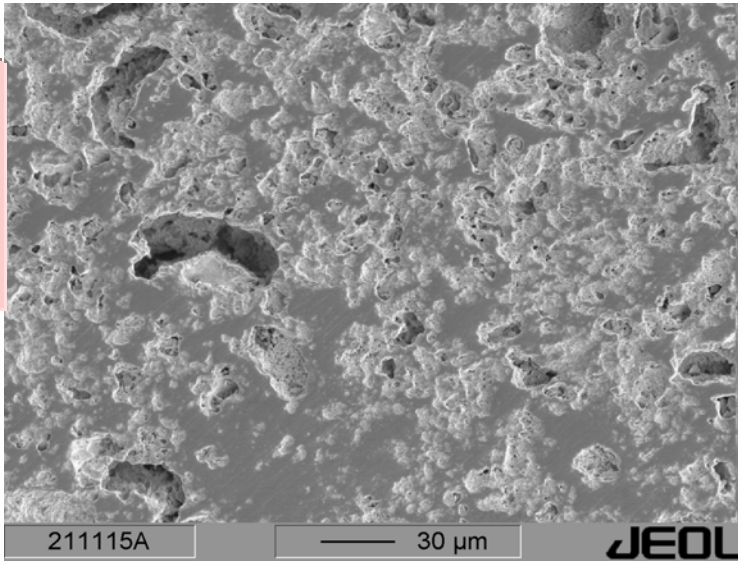


9.1 [wt%] Al



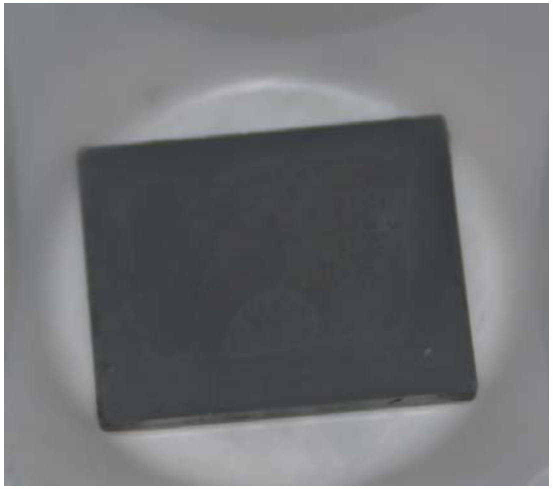


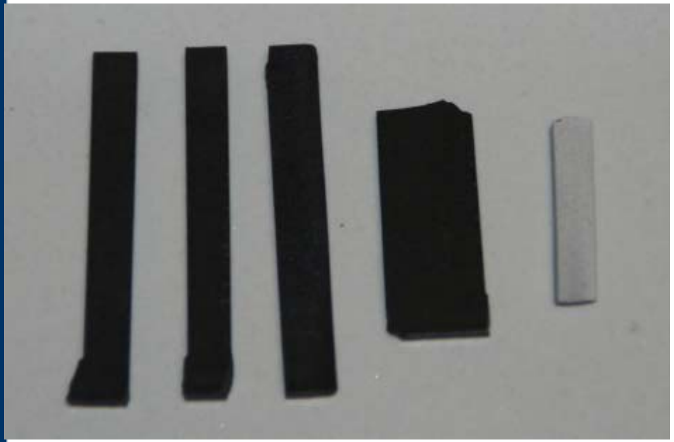
16.6 [wt%] Al

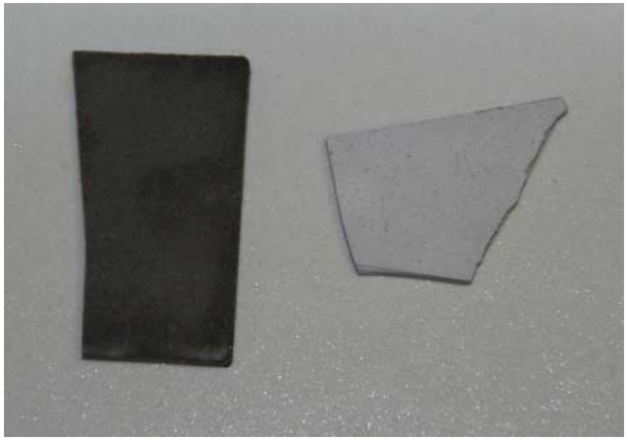


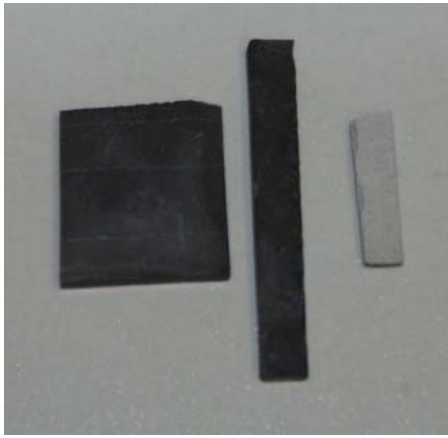
1300°C

1500°C









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Summary

❖ Modification of commercially available polysiloxane (MK Polymer) with aluminum (aluminium oxide, aluminium nanopowder) followed by pyrolysis results in bulk Si-Al-O-C ceramics with no Cristobalit phase separation.

❖ Post pyrolysis heat treatment of the prepared bulk Si-Al-O-C ceramics result in SiC-Mullite composite materials in which the Cristobalit phase is not present.

❖ The prepared bulk Si-Al-O-C ceramics are showing no post-pyrolysis cracks.

❖ Crystallization of β-SiC and Corundum is observed for bulk Si-Al-O-C ceramics (MK Polymer + Al, Al/Al_2O_3).

❖ Mullite formation is observed for all bulk Si-Al-O-C ceramics (one exception: MK Polymer + Al [28.57 wt%]).

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Conclusions

- The corrosion protection of the bulk Si-Al-O-C ceramics will improve compare it with the bulk Si-O-C ceramics as we do not observe the Cristobalit phase separation.

- Mechanical properties (strength, toughness) of the bulk Si-Al-O-C ceramics will improve compare it with the bulk Si-O-C ceramics.

- Electrical properties of the bulk Si-Al-O-C ceramics will improve compare it with the bulk Si-O-C ceramics (lower free carbon content value).

Future work

- To use modified surface aluminium oxide fillers.

- To improve the working conditions with the warm press.

- To use $MoSi_2$ as filler to study its influence on the electrical properties of the bulk Si-Al-O-C ceramics

- To gather as many data which will be use in building of a statistic work plan.

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Acknowledgements

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