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Recent
CMAS related activities at IEK-1

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PROVIDA Meeting, April 1st, 2015, Cambridge, UK

Summary of Interests

- Materials synthesis and processing
  for advanced (thermally sprayed) TBC systems
- Corrosion gradient burner rig testing
- TBC degradation under simultaneous load
  - *Degradation of structural integrity*
  - *Impact of microstructure*
  - *Impact of cycling frequency and deposition rate*
  - *Impact of chemistry , mitigation in advanced ceramics*
- Development of CMAS tolerant TBC systems

Burner Rig Testing

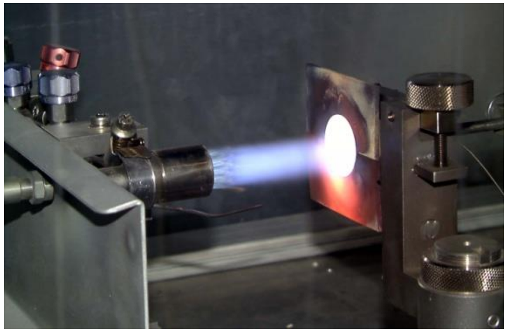
Thermomechanical cycling

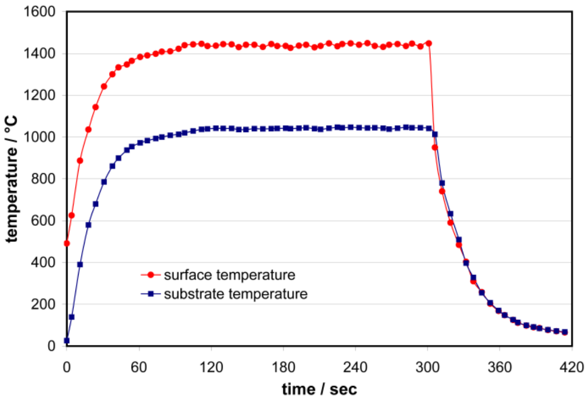
- Natural gas / oxygen burner
- Compressed air cooling (backside & front)
- Cyclic heating & cooling

Typical lifetime w/o CMAS deposit for advanced YSZ TBC

- >2000 cycles at $T_{surface}$ = 1250°C
- >800 cycles at $T_{surface}$ = 1400°C

with $T_{bondcoat}$ ≈1080°C and 5min heating, 2min cooling





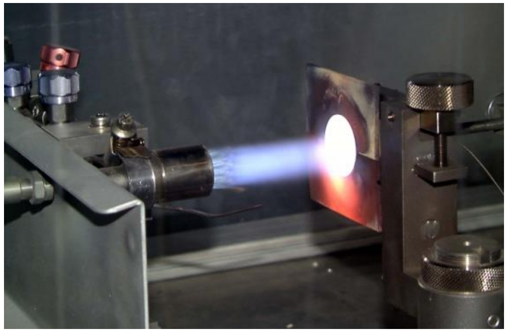
CMAS Burner Rig Testing

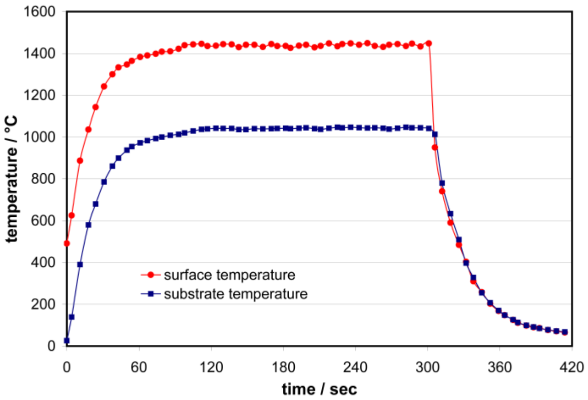
Thermomechanical cycling

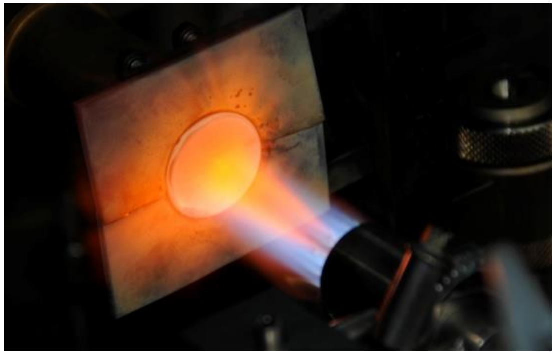
- Natural gas / oxygen burner
- Compressed air cooling (backside & front)
- Cyclic heating & cooling

Continuous deposition simulated as during engine operation

- CMAS solution directly injected and atomized into the burner flame
- Orange discoloration visible (alkalides)



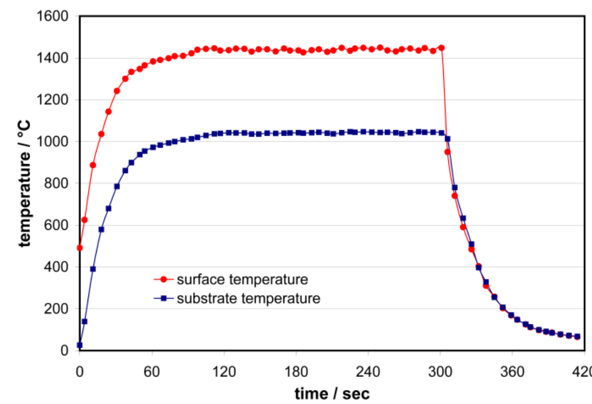




Variation of Load Conditions

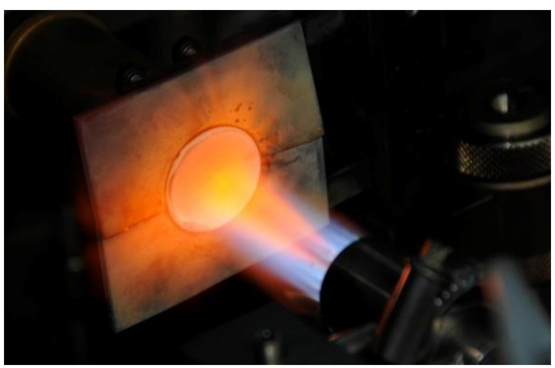
A number of parameters to be controlled …

- Surface temperature
- Temperature gradient
- High temperature dwell time
- Cycling frequency
- CMAS composition
- Feeding rate



… to influence

- Melting, viscosity of deposit
- Reaction kinetics
- Phase formation
- Thermomechanical stresses
- Crack formation and growth
- Oxidation, sintering
- …



CMAS Arrest & Mitigation
Advanced TBC and Plant Deposits

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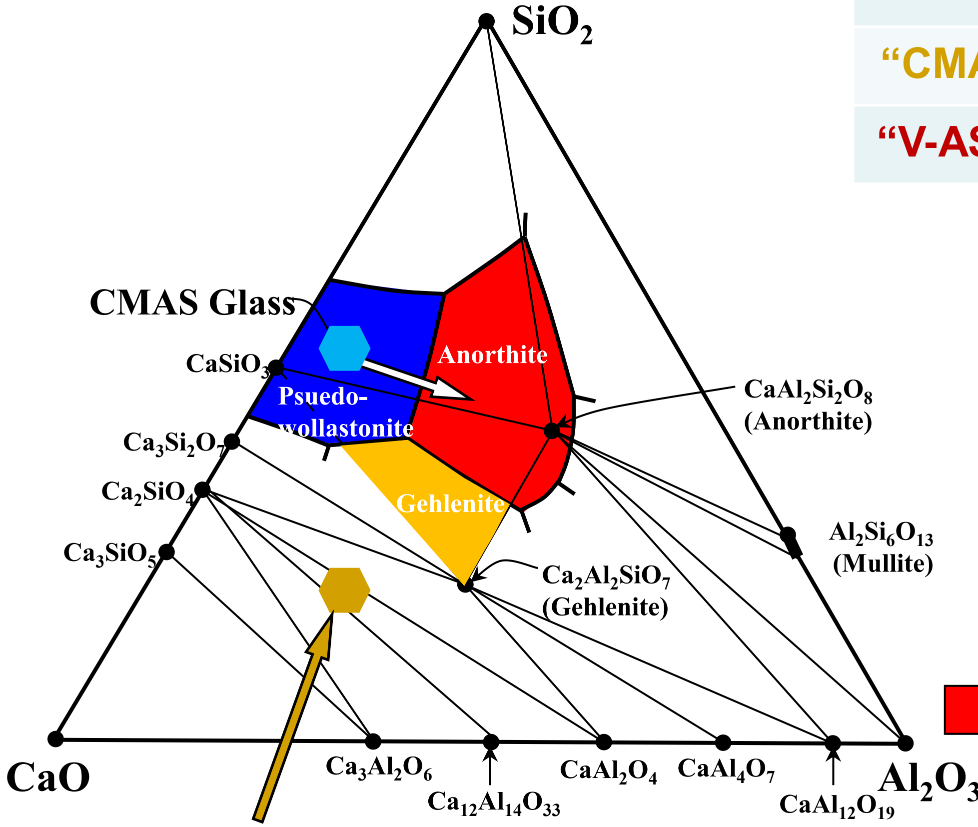
Psuedowollastonite Field
Difficult to Crystallize



Plant „CMAF“ Deposit

	Ca	Mg	Al	Si	Fe	Na	K
“CMAS”	38	5	4	50	1	1	1
“CMAF”	26	11	9	13	43	0	0
“V-ASH”	..	..	..	..	..	..	..

Cation fractions in solutions (mol%)

also variants with additions of sulphur, titania, ..

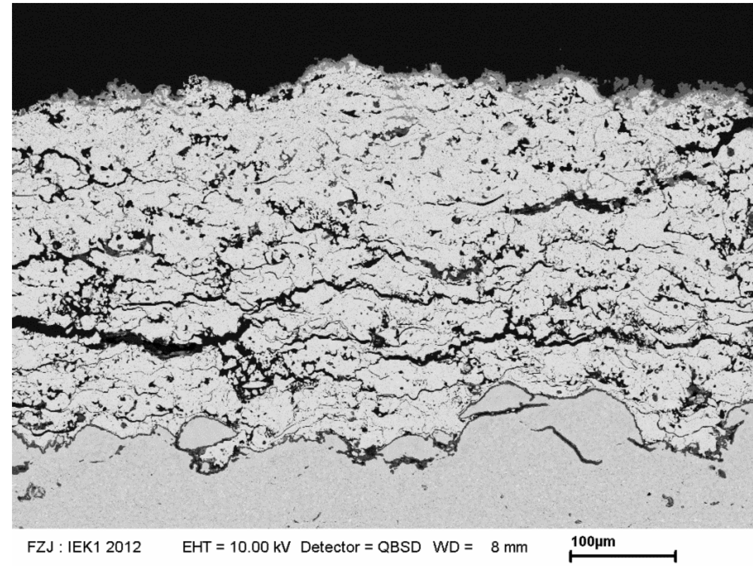
Anorthite & Gehlenite Field
Easy to Crystallize (with Al^{3+}/Ti^{4+}/Gd^{3+})

…Padture *et al.*, *Acta Mater.*, 2007

Gradient Rig CMAS Invasion: APS

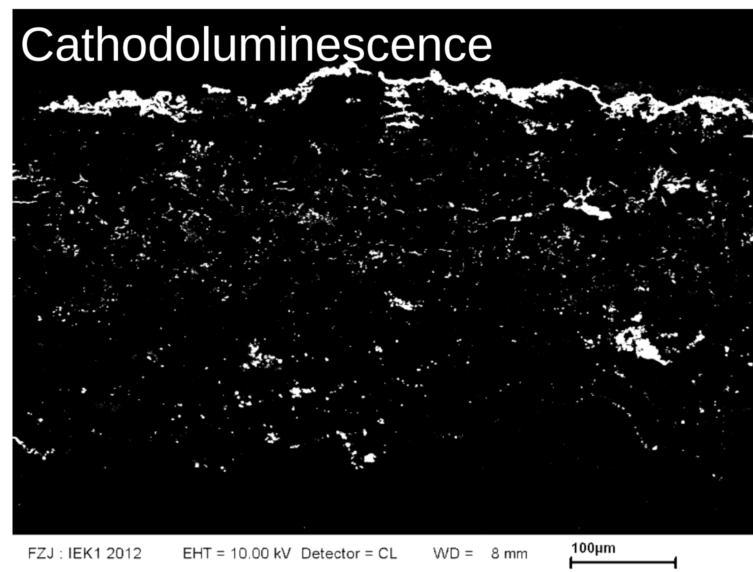
<u>Test conditions:</u>

$T_{surface}$: 1250°C
Deposit: „CMAS“
Rate: 0,12mg/min
Dwell time: 1x (5/2)



Cycles to failure ≈ 160 cycles
Time to failure ≈ 13,3 hours

- Top-down infiltration of porosity (along large cracks)
- Dissolution /Re-precipitation of YSZ
- Sparse invasion (preferred in large voids)



Gradient Rig CMAS Invasion: APS

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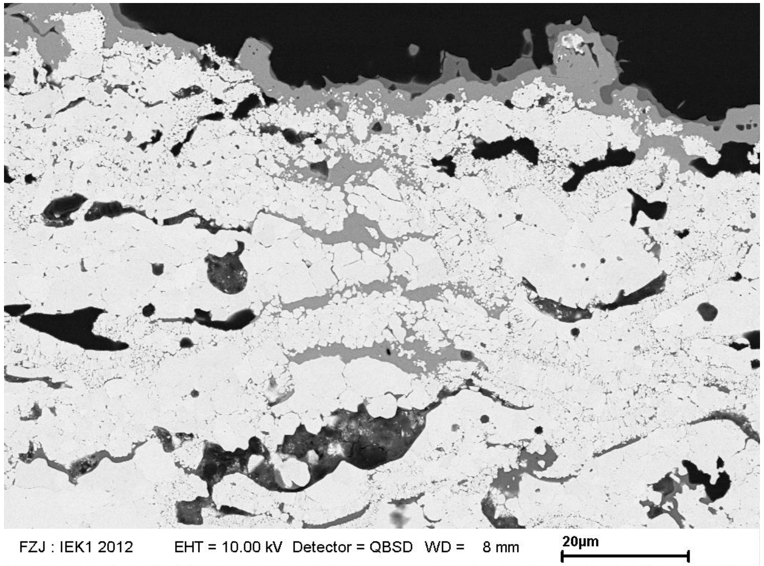
Deposit: „CMAS“
Rate: 0,12mg/min
Dwell time: 1x (5/2)



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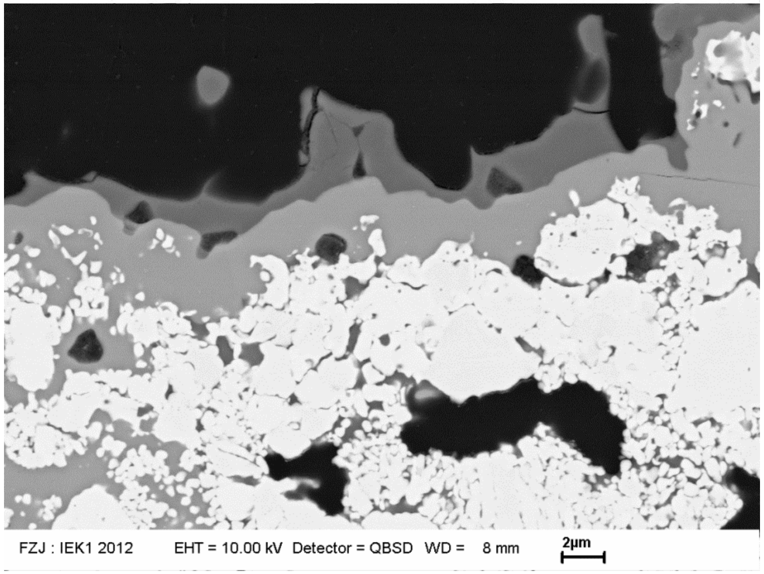

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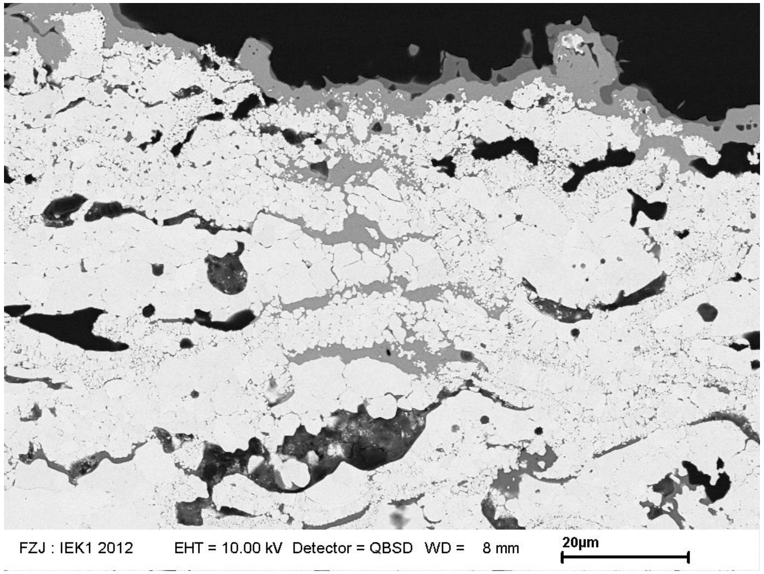

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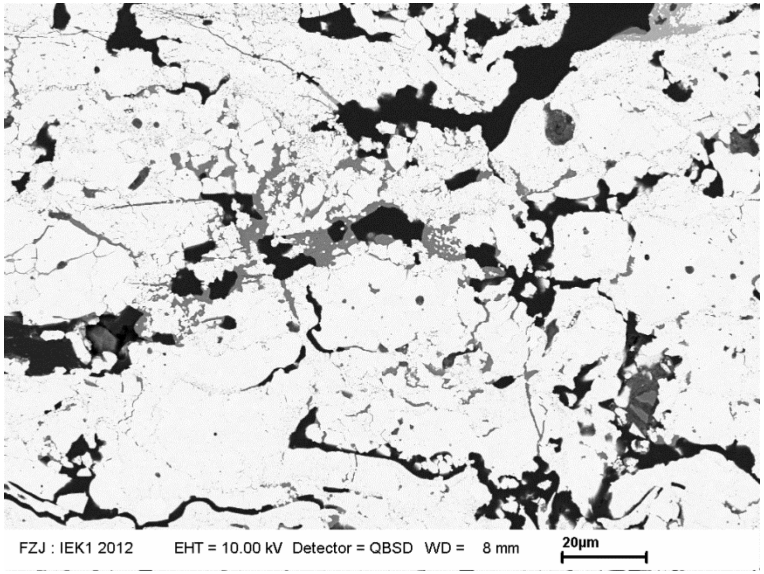


Impact of Different Dwell Times

- State of the art YSZ TBC
- Test conditions:
  - *$T_{surface}$: 1250°C*
  - *Deposit: „CMAS“*
  - *Deposition rate: 0,45mg/min*
  - *Dwell times:*

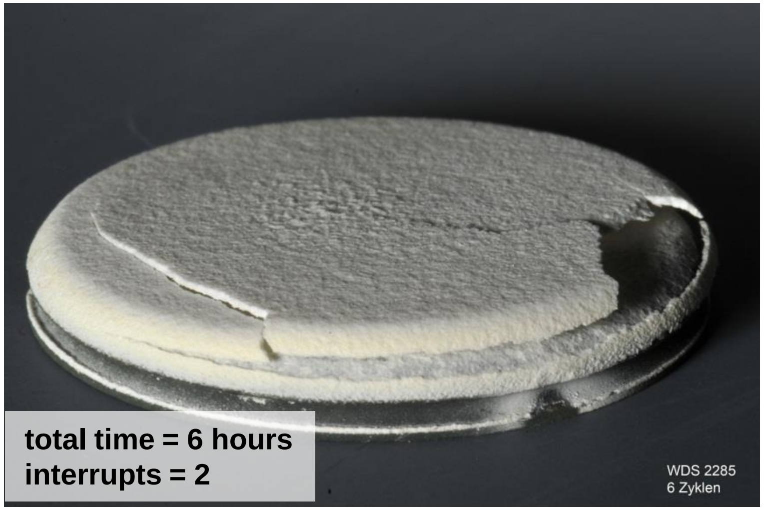
    1x (5/2)

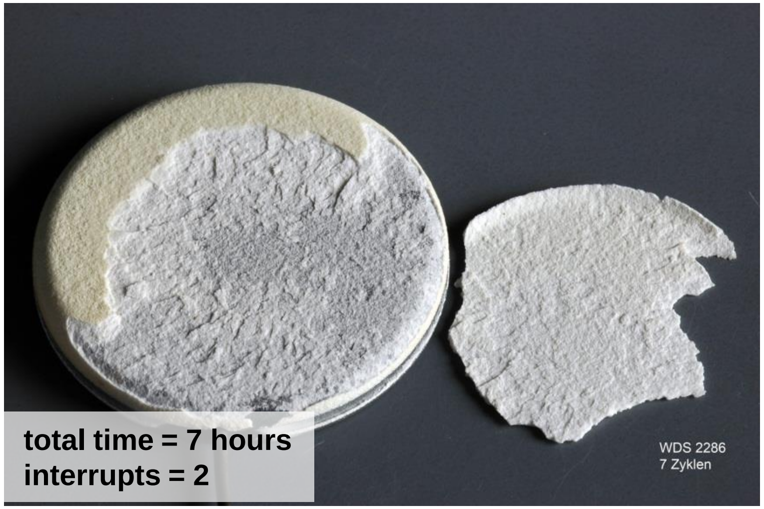
    5x (25/10)

    10x (50/20)
- Degradation of TBC with flake like defoliation as often observed with CMAS

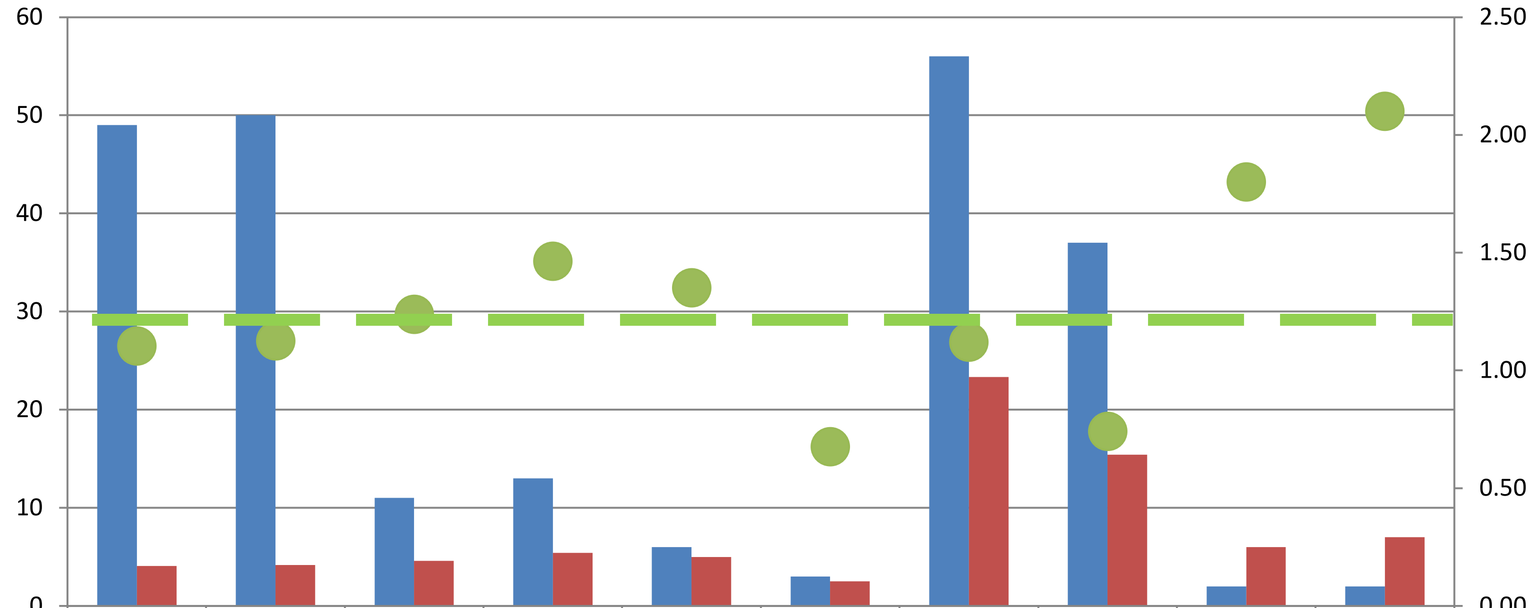
Non-Cyclic Loading

- State of the art YSZ TBC
- Test conditions:
  - *$T_{surface}$: 1250°C*
  - *Deposit: „CMAS“*
  - *Deposition rate: 0,5 mg/min)*
  - *Dwell time: unlimited (only accidential interrupts)*
- Delamination of TBC not flaky but „en bloc“ near bondcoat
- Delamination occurs on heating ramp unlike usual in TGO derived failure





Summary on
Dwell Time and Deposition Rate

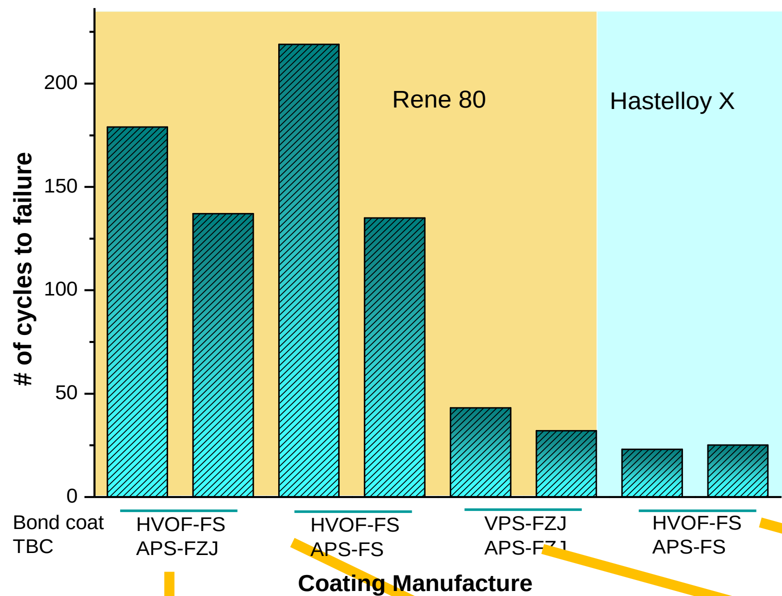


	H=5min, C=2min, CMAS 0,45mg/min	H=5min, C=2min, CMAS 0,45mg/min	H=25min, C=10min, CMAS 0,45mg/min	H=25min, C=10min, CMAS 0,45mg/min	H=50min, C=20min, CMAS 0,45mg/min	H=50min, C=20min, CMAS 0,45mg/min	H=25min, C=10min CMAS 0,08mg/min	H=25min, C=10min CMAS 0,08mg/min	H>>60min, C=Accid. CMAS 0,50mg/min	H>>60min, C=Accid. CMAS 0,50mg/min
Cycle to failure	49	50	11	13	6	3	56	37	2	2
Total deposition time (h)	4.1	4.2	4.6	5.4	5.0	2.5	23.3	15.4	6.0	7.0
Accumulated deposit (g)	1.10	1.13	1.24	1.46	1.35	0.68	1.12	0.74	1.80	2.10

- Accumulated deposit apparently most important load factor !

1.

High temperature corrosion with CMAS @ 1250°C



CMAS composition (mol%)

Ca	Mg	Al	Si	Fe	Na	K
38	5	4	50	1	1	1

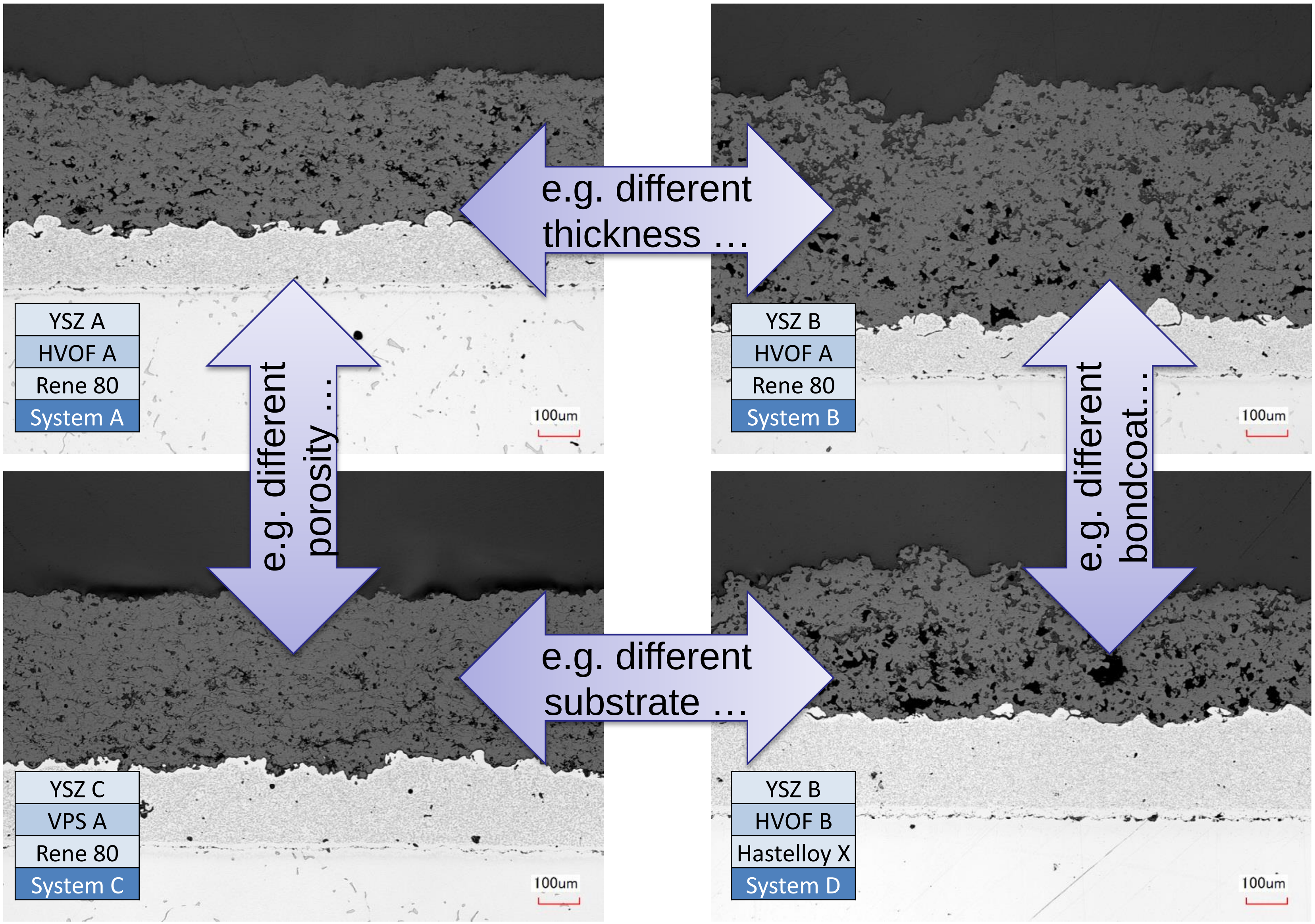
- Failure occured within the YSZ TBC and bondcoat interface
- Tests have been finished and characterization is on-going

Surface T / Substrate T, °C	**1261 / 1045**	**1256 / 994**	**1239 / 1040**	**1218 / 982**
Porosity of TBC (as-sprayed), %	**15**	**16**	**15**	**No info.**
BC Roughness, um	**10.3 / 13***	**10.2**	**13.2***	**No info.**

*** FZJ measurement**

e Chemistry but…

Micrographs after 400 burner rig cycles (5min/2min at 1250°C / 1080°C)



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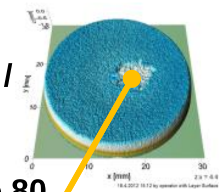
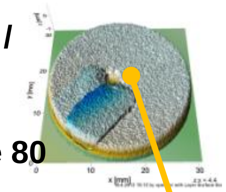
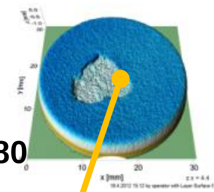
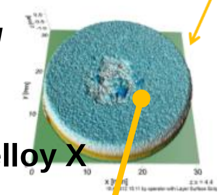
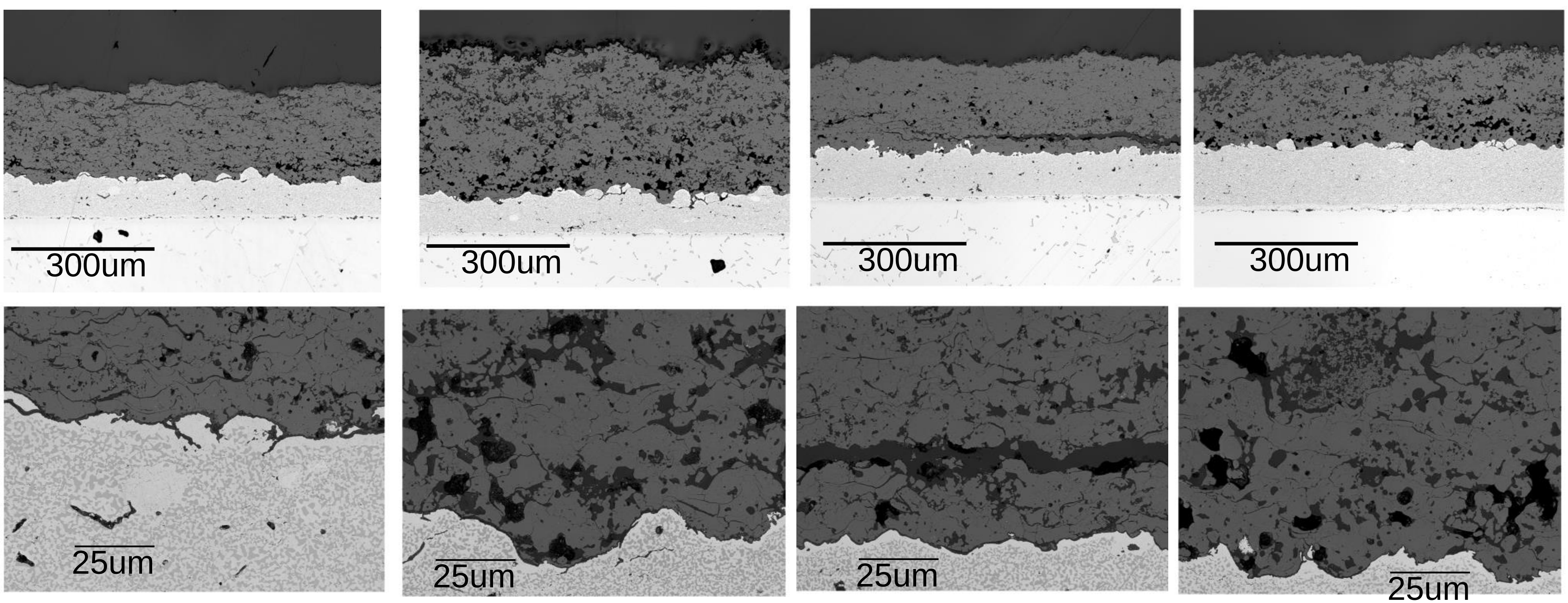
High temperature corrosion with CMAS @ 1250°C

BC / TBC Manufacturer	HVOF-FS / APS-FZ	HVOF-FS / APS-FS	VPS-FZ / APS-FZ	HVOF-FS / APS-FS
Surface T / Substrate T, °C	1261 / 1045	1256 / 994	1239 / 1040	1218 / 982
Lifetime	179	219	32	25
Substrate	Rene 80	Rene 80	Rene 80	Hastelloy X

Area of microscopic observation

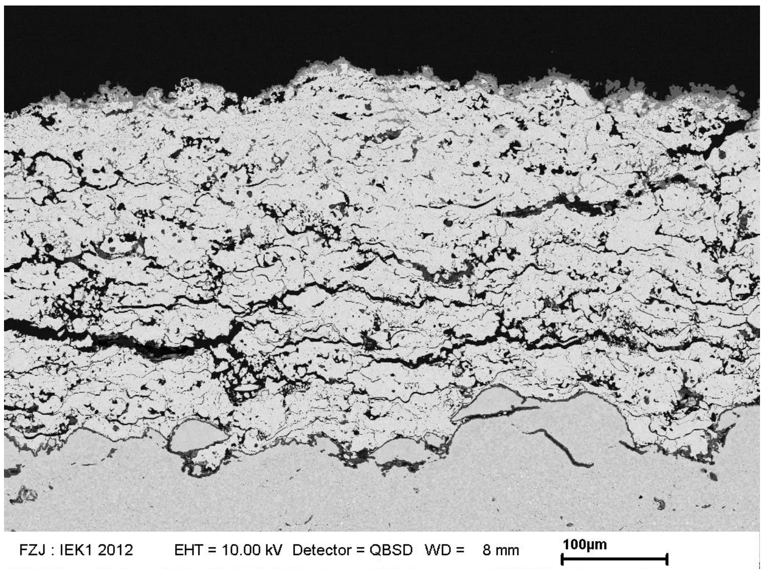


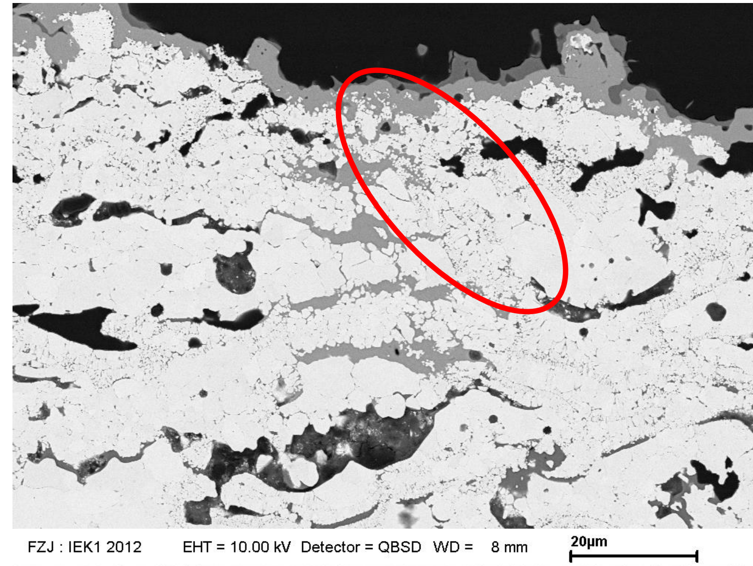
Cross-section micrographs of tested samples

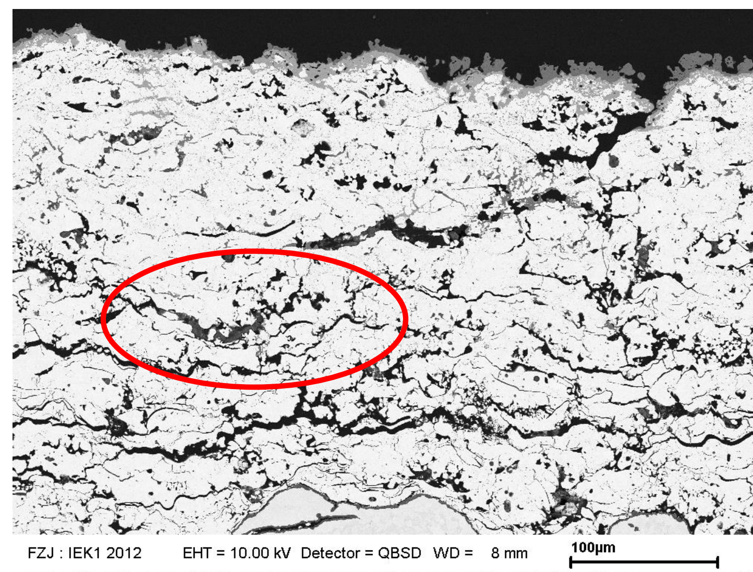
System A

ctf ≈ 160 cycles

YSZ A
HVOF A
Rene 80
System A







- *re-precipitation of YSZ*
- *sparse infiltration preferred in large voids*

System B

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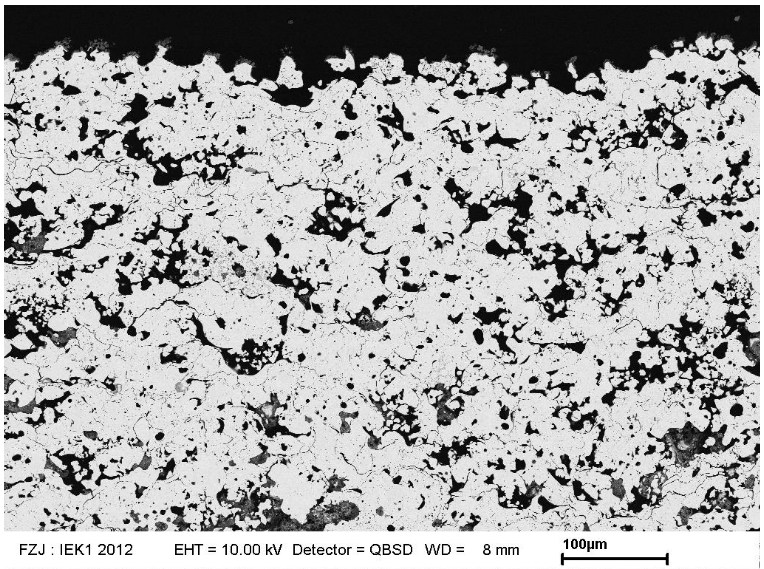
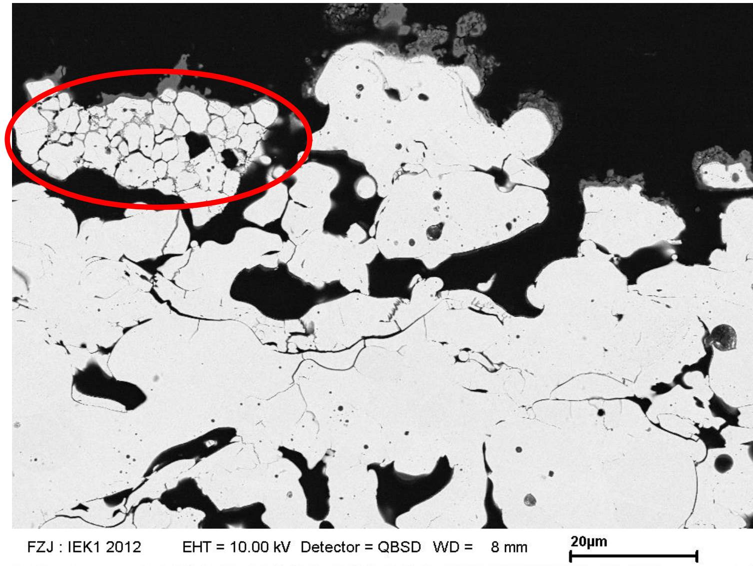
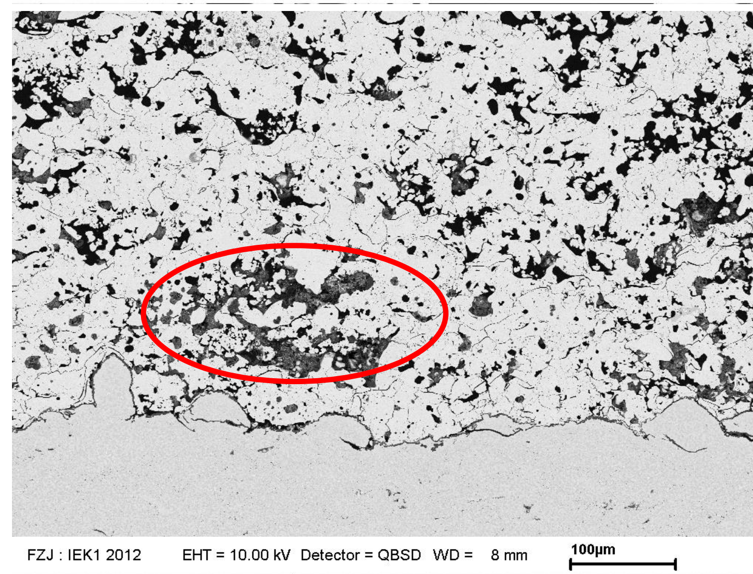
ctf ≈ 180 cycles

YSZ B
HVOF A
Rene 80
System B





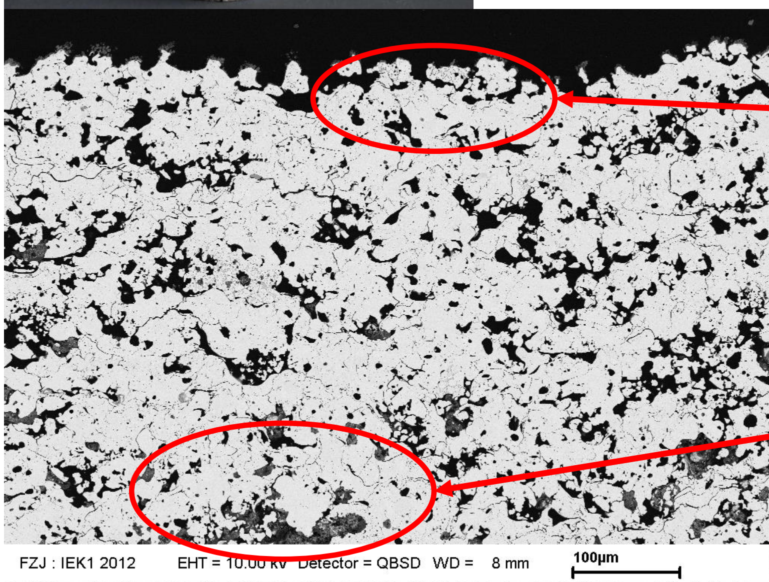


- *re-precipitation of YSZ*
- *sparse infiltration preferred in large voids*

Compare System B vs. D

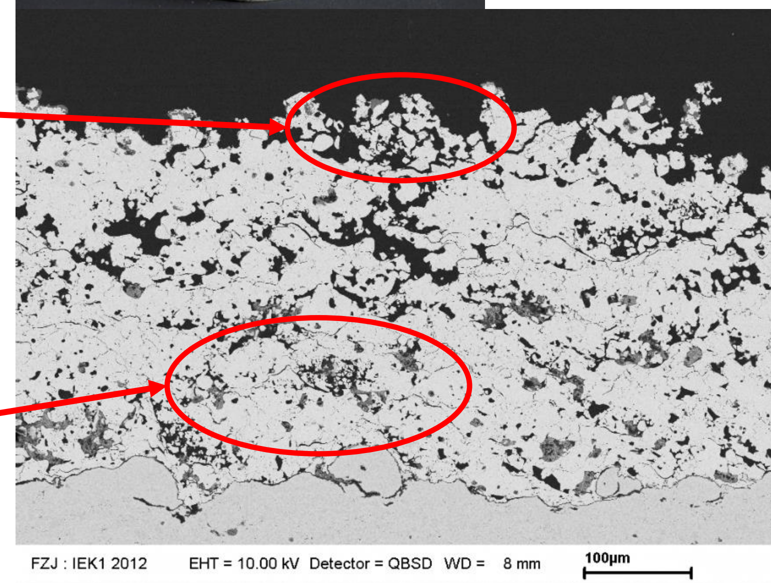
ctf ≈ 180 cycles

YSZ B
HVOF A
Rene 80
System B



ctf ≈ 25 cycles

YSZ B
HVOF B
Hastelloy X
System D



Different degradation potentially due to different stress levels

- Layer thickness, interface temperature
- Substrate material
- Interface roughness

General comments:

- Major impact of microstructure (porosity, pore size) on performance and damage mode (shallow, spallation or in-depth delamination)
- Mechanism of in-depth degradation still insufficient understood

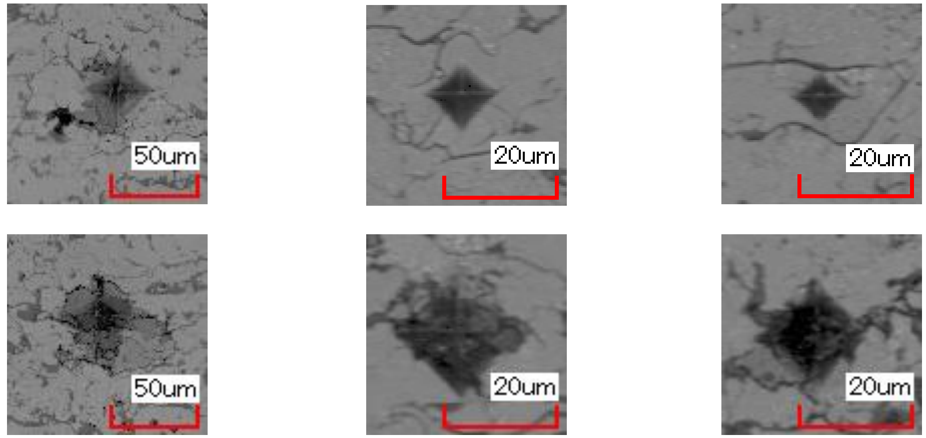
- Started some work on evolution of CMAS induced degradation by „interrupted“ cycling tests
  - same kind of YSZ TBC system
  - same test conditions
  - test not driven to failure for all specimen
  - characterization of mechanical degradation by indentation testing
  - started some modelling to describe

Vorversuche – Last

5000mN | 1000mN | 500mN

„Gute“ Eindrücke

„Schlechte“ Eindrücke

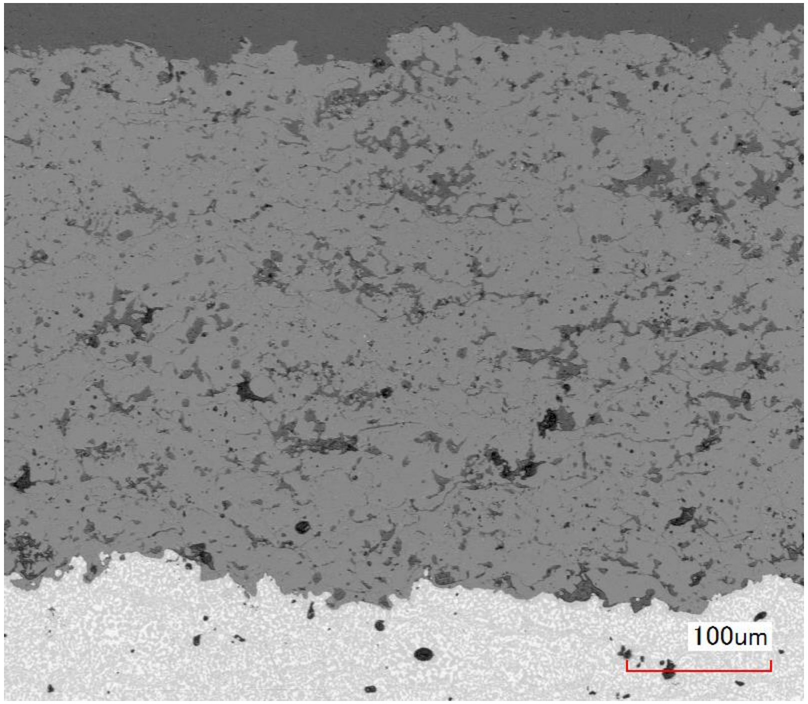


HEL0001 (TPro; CMAF) – konf. Lasermikroskop

- höhere Last → größere Eindrücke → größeres Prüfvolumen → besser für Statistik;
  aber auch mehr und evtl. ungewollte Defekte im Prüfvolumen (Poren)
- **wichtig:** höhere Last → niedrigere gemessene Härte (Indentation Size Effect); auch strukturabhängig → Vergleich versch. Lasten/Mikrostrukturen schwierig

➢ **Idee:** Prüfkraft an Mikrostruktur und gewünschter Defektgröße anpassen
➢ **Frage:** Welche Defekte sind für den Einfluss von CMAS/CMAF zu berücksichtigen?

Serie 1 – Indentation



HEL0028 (as-sprayed)
konf. Lasermikroskop

TBC: Standard YSZ APS

BC: Amdry386 VPS

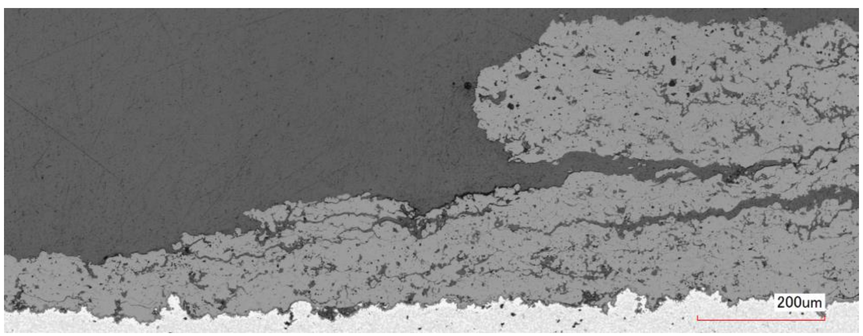
Sub: IN738

Force: 250mN

→(Indent < Splat)

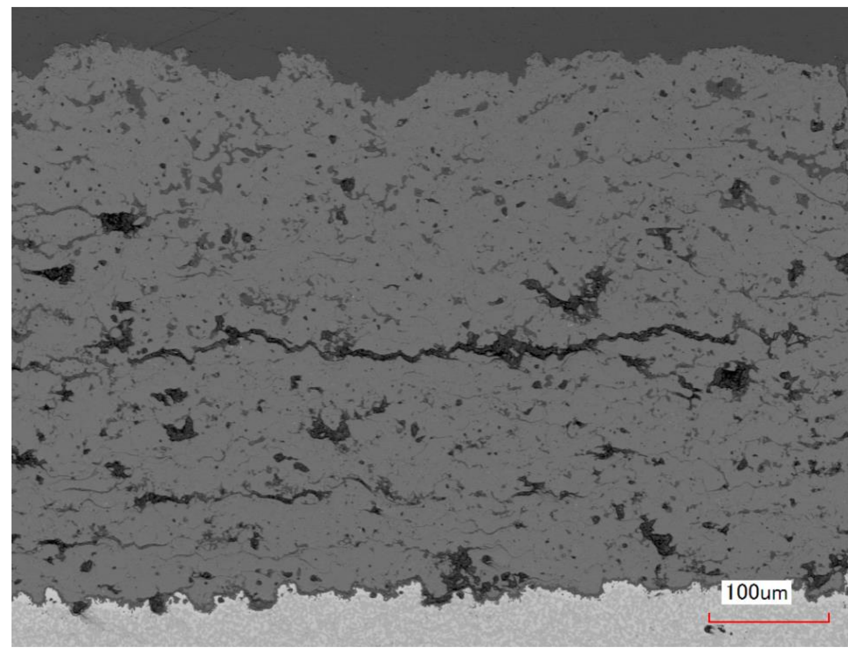
Serie 1 – Failure and Degradation

TBC delaminates near BC



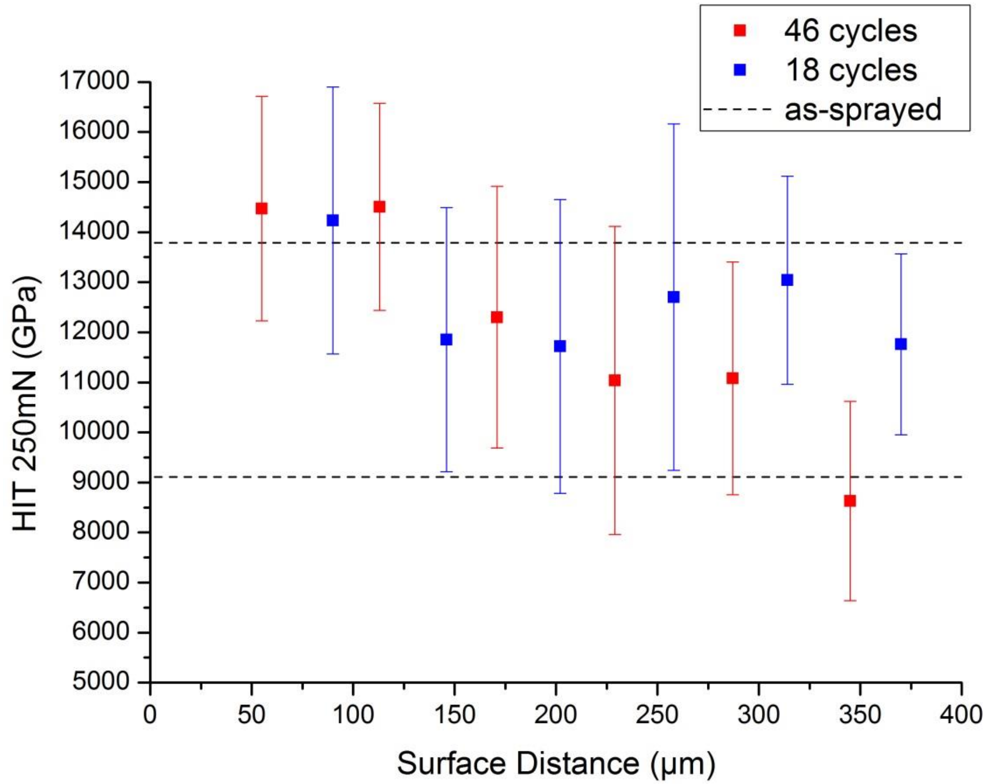
HEL0023: 69 Zyklen, versagt
konf. Lasermikroskop

Horizontal cracks in central and upper levels



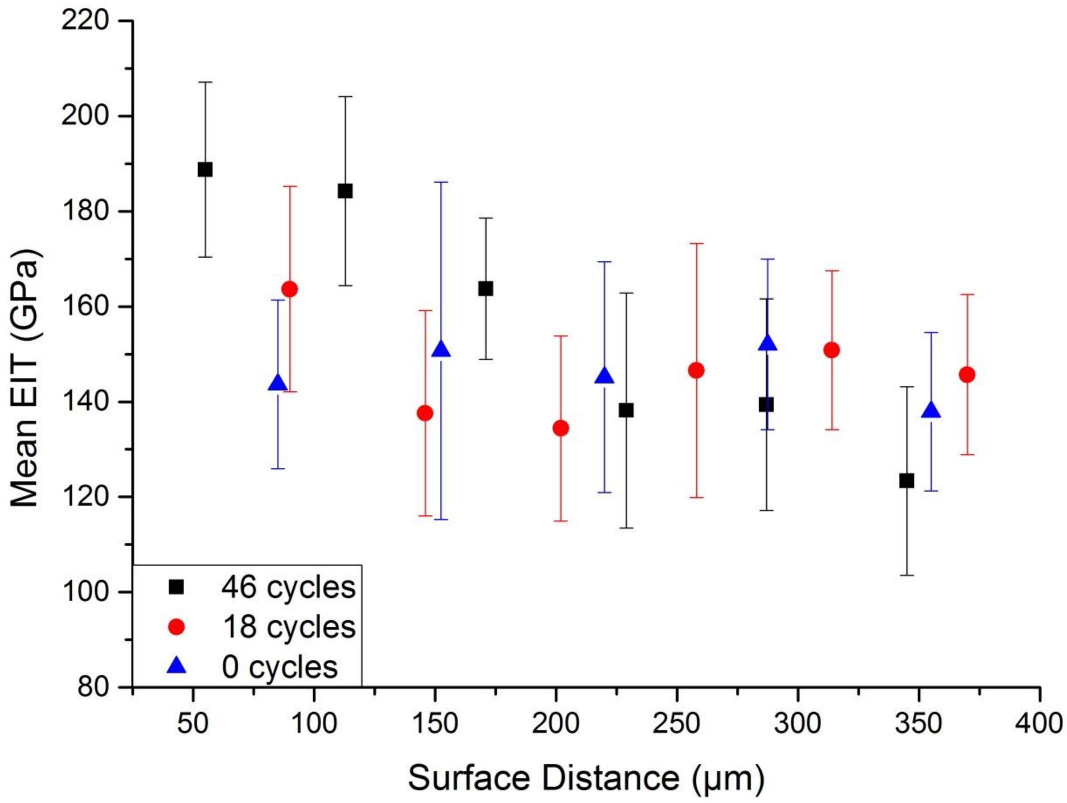
HEL0024: 46 Zyklen, intakt
konf. Lasermikroskop

Serie 1 – Indentation Results



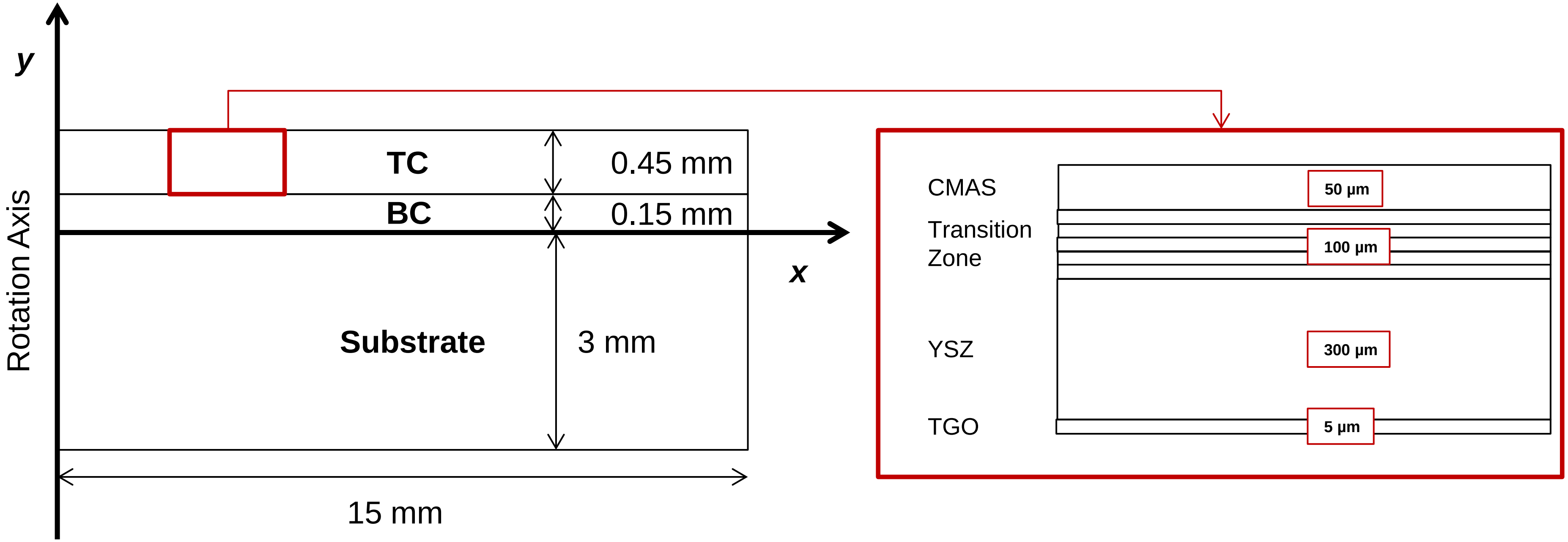
- expected trend of increased hardness in surface near region
- is there hardness drecrease near BC interface

Serie 1 – Indentation Results

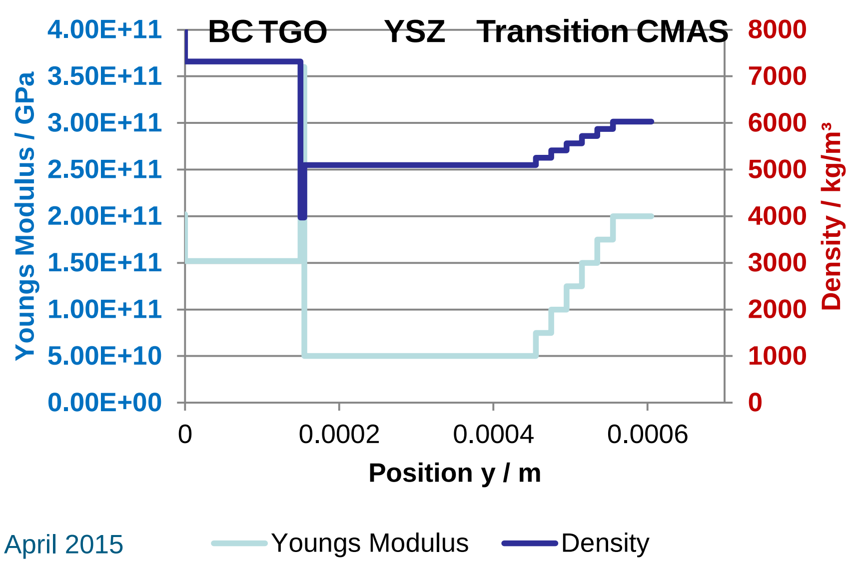


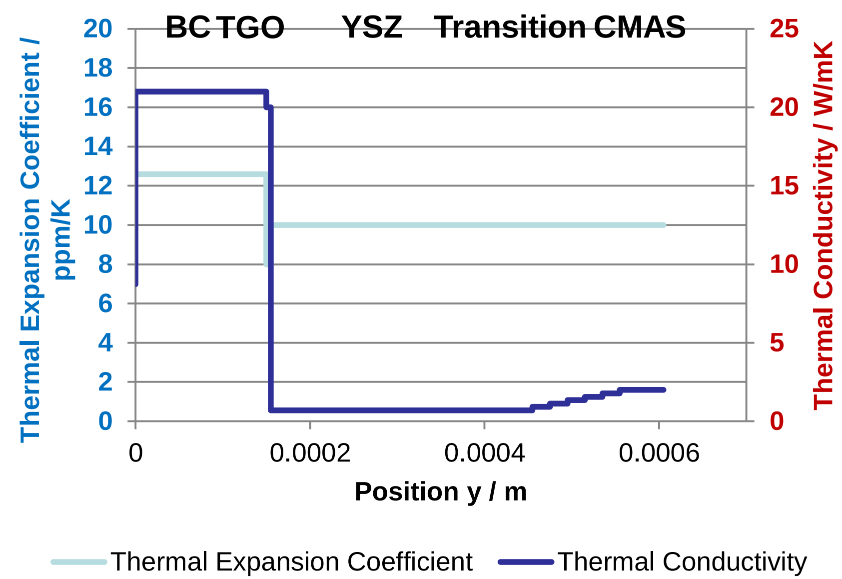
- Similar trend for Young‘s modulus

Modelling: Geometry and Material Parameter

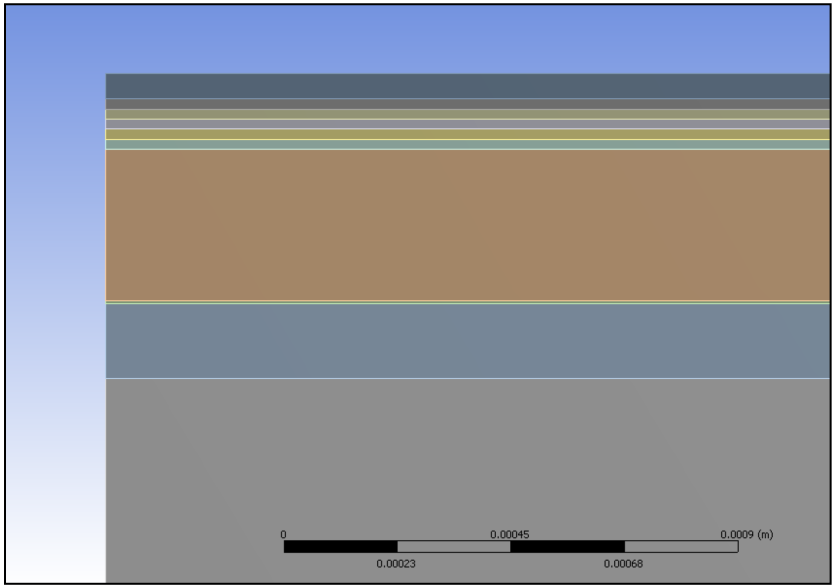


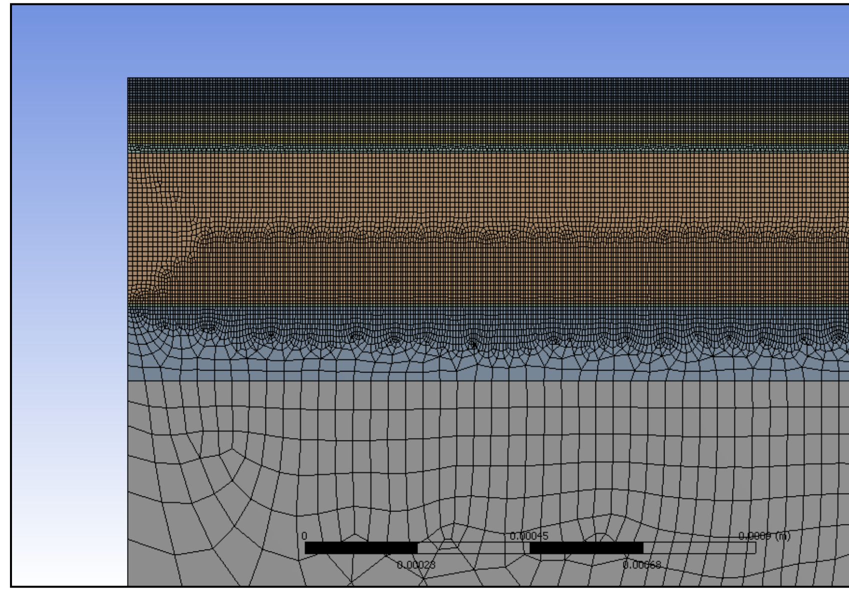
Material Parameter at Room Temperature:





Modelling: Meshing and Boundary Conditions





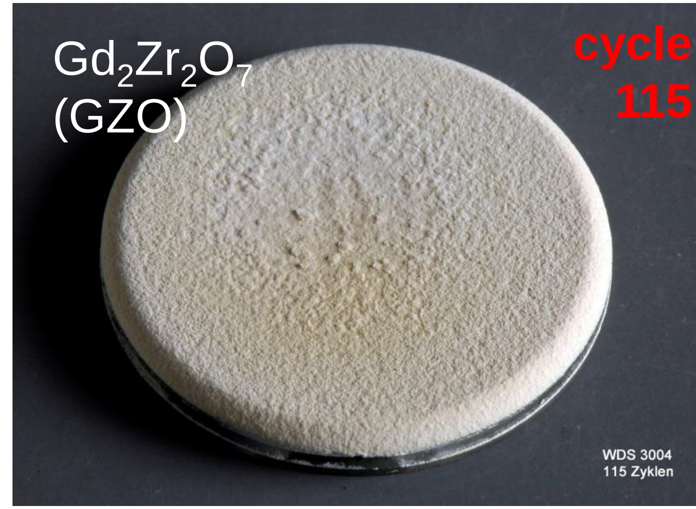
Thermal Boundary Conditions	
Case 1	**Case 2**
Isothermal 1000 °C Cooling to 22 °C	Heating: Convection (h = 2000 W/m²K, T = 1450 °C) Cooling: Convection (h = 350 W/m²K, T= 22 °C)
Mechanical Boundary Conditions	
Restriction of displacement at substrate bottom center	

Happy for comments….

Advanced TBCs for CMAS Mitigation

Assessment: ~80 cycles CMAS @ 0,12mg/min

Deep exfoliation of YSZ reference



Improved resistance for advanced double layer ceramics with mitigation within advanced ceramic surface near layer