EINFLUSS VON WASSERDAMPF AUF HOCHTEMPERATURBESCHICHTUNGEN

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ÜBERBLICK

Einleitung

Schutzschichten für Faserverbundwerkstoffe (EBCs)

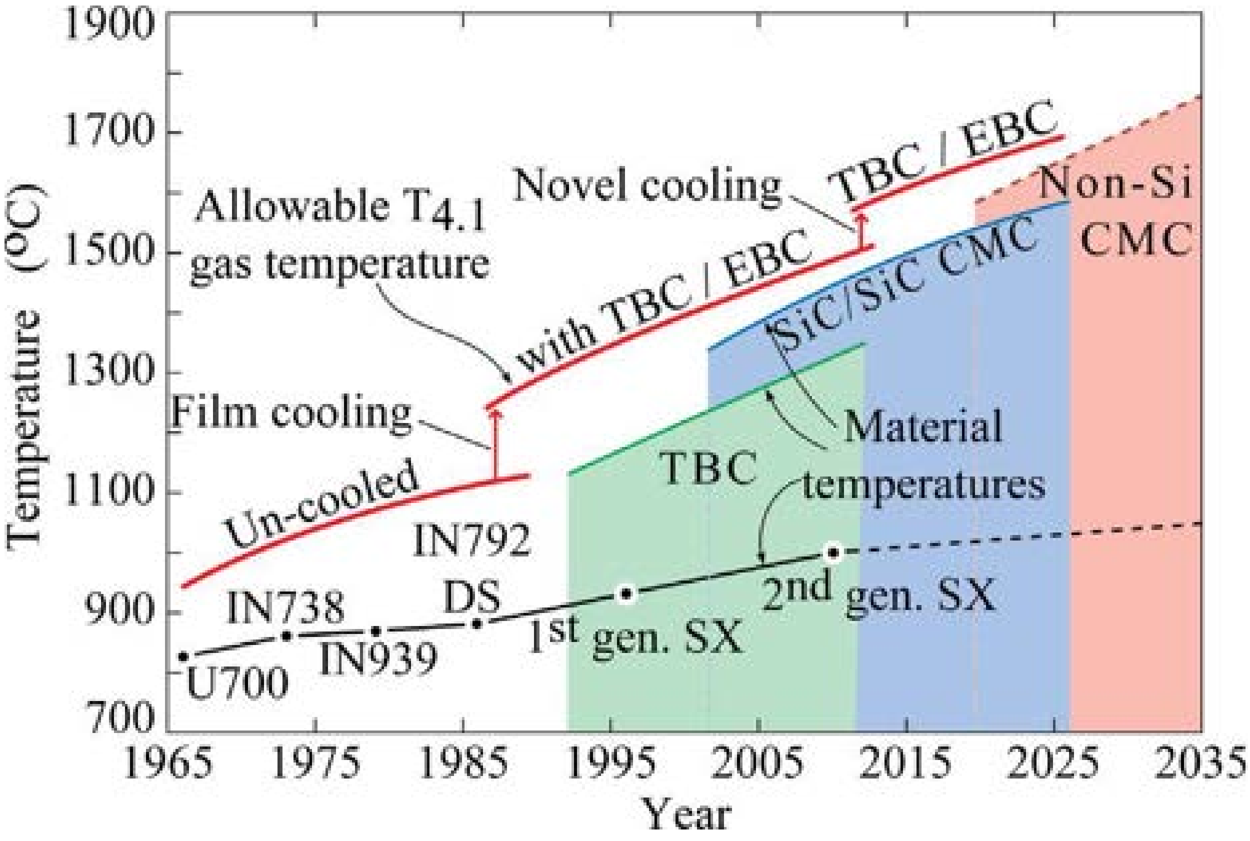
Vorstellung unterschiedliche Testmöglichkeiten:

- Gasbrenner
- IKTS-Rig
- HVOF-Brenner

Einfluss von Wasserdampf auf Wärmedämmschichten

Zusammenfassung

EINLEITUNG – BETRIEBSTEMPERATUREN GASTURBINEN



Verbesserte Effizienz/Lebensdauer von Gasturbinenkomponenten durch:

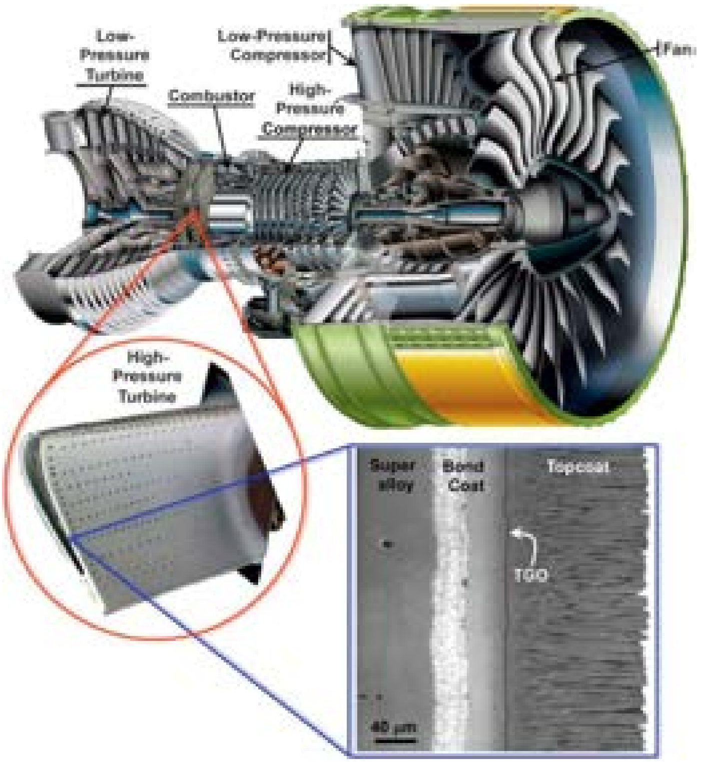
Wärmedämmschichten (WDS) / Thermal Barrier Coatings (TBCs)

Faserverbundwerkstoffe / Ceramic Matrix Composites (CMCs)
+
Schutzschichten / Environmental Barrier Coatings (EBCs)

B. T. Richards, H. N. G. Wadley, Journal of the European Ceramic Society 2014, 34, 3069-3083.

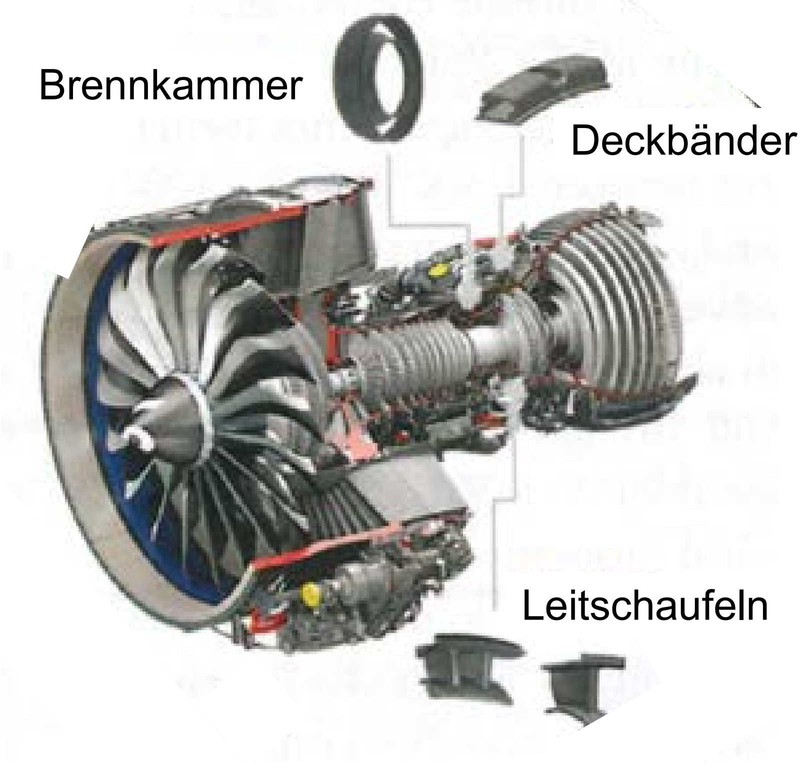
EINFÜHRUNG – GASTURBINEN-BESCHICHTUNGEN

Nickel Basis Superlegierungen plus Wärmedämmschichten/Thermal Barrier Coatings (WDS/TBCs)



D.R. Clarke, M. Oechsner, N.P. Padture, MRS Bulletin, 37 (2012) 891-898.

Keramische Faserverbundwerkstoffe (CMCs) plus Schutzschichten/Environmental Barrier Coatings (EBCs)



Brennkammer

Deckbänder

Leitschaufeln

J. Steibel, American Ceramic Society Bulletin 98, 3 (2019) 30-33.

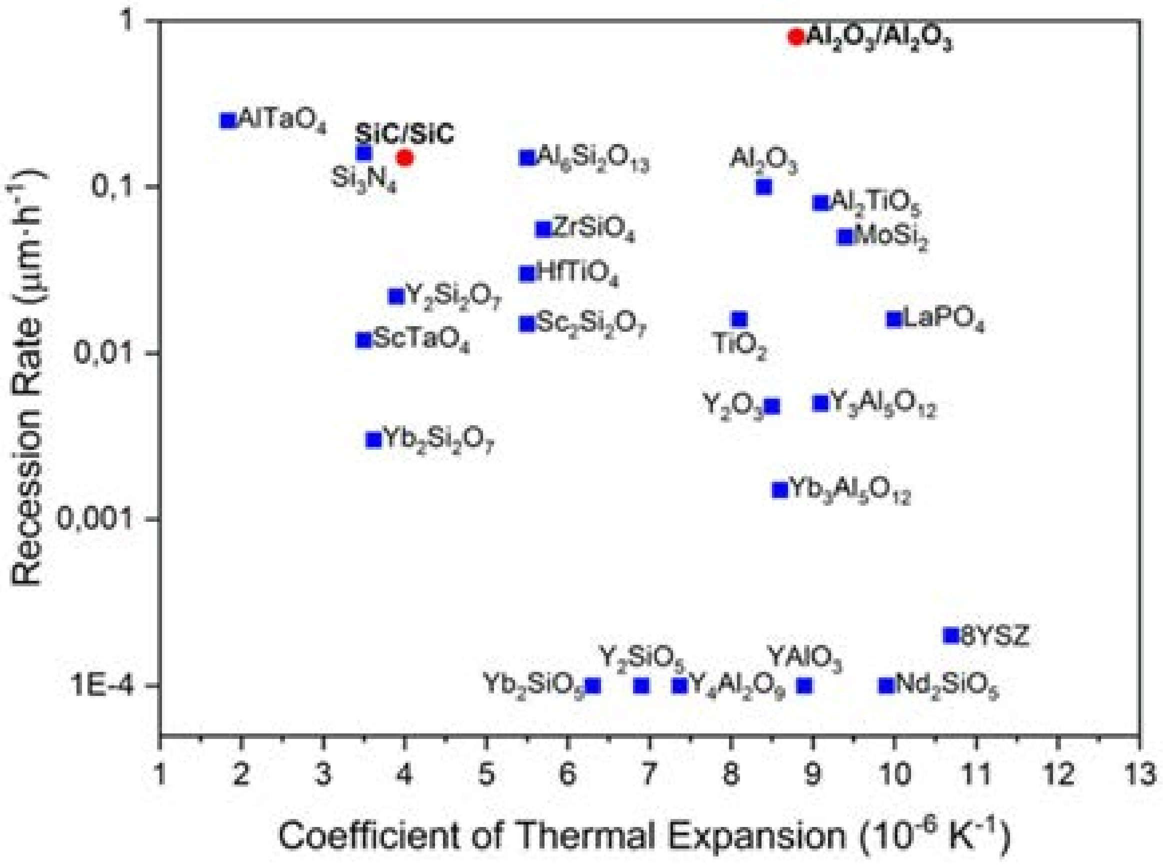
ENVIRONMENTAL BARRIER COATINGS (EBCS)

Auswahlkriterien für EBCs:

- Exzellente Korrosionsbeständigkeit
- Thermische und chemische Stabilität
- Gute Anbindung
- Geringer Ausdehnungskoeffizientunterschied $\Delta\alpha$ zum Substrat:

  Energiefreisetzungsrate:

$$G = \frac{\sigma^2 h}{2E_{EBC}} \propto E_{EBC}\, h\, \Delta\alpha^2$$



*M. Herrmann, H. Klemm, Comprehensive Hard Materials **2014**, 2, 413-446.*

ALTERUNG VON SCHUTZSCHICHTEN (EBCS)

Reaktion Wasserdampf mit SiC

SiC bildet bei hohen Temperaturen eine schützende SiO_2 Schicht

$\mathbf{SiC(s)} + 3H_2O(g) \rightarrow \mathbf{SiO_2(s)} + 3H_2(g) + CO(g)$

SiO_2 verflüchtigt sich in schnellem Wasserdampf (wie viele Oxide)

$\mathbf{SiO_2(s)} + 2H_2O(g) \rightarrow \mathbf{Si(OH)_4(g)}$

Die schnelle Entfernung der Reaktionsprodukte bewirkt eine sichtbare Degradation, für die Diffusion durch die Grenzschicht unterscheidet man zwischen laminaren und turbulenten Bedingungen:

$$k_{laminar} = a.\,exp\left(\frac{-E}{RT}\right).\,v^{1/2}\,.\,(P_{H_2O})^n.\,P^{-1/2}$$

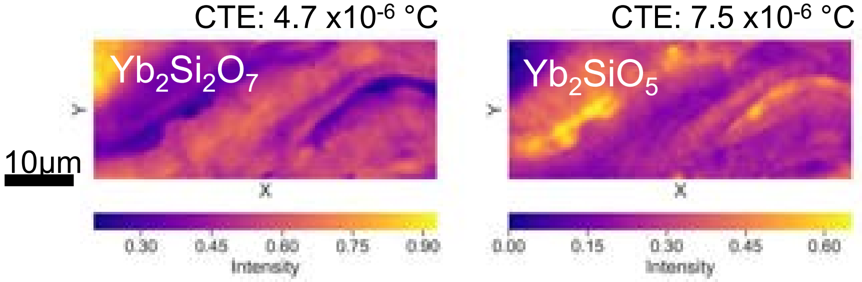
$$k_{turbulent} = a.\,exp\left(\frac{-E}{RT}\right).\,v^{4/5}\,.\,(P_{H_2O})^n.\,P^{-1/5}$$

E. J. Opila et al., J. Am. Ceram. Soc., 1999

EBCS ÜBER THERMISCHE SPRITZTECHNOLOGIEN

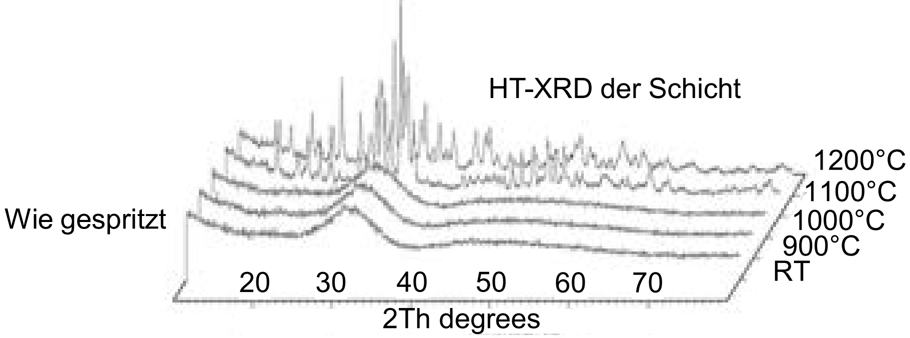
Problemstellungen bei der Schichtherstellung:

- **Zweitphasen** (Yb_2SiO_5) in $Yb_2Si_2O_7$ Lagen mit hohem CTE durch hohe Prozesstemperaturen (Si-Verlust)

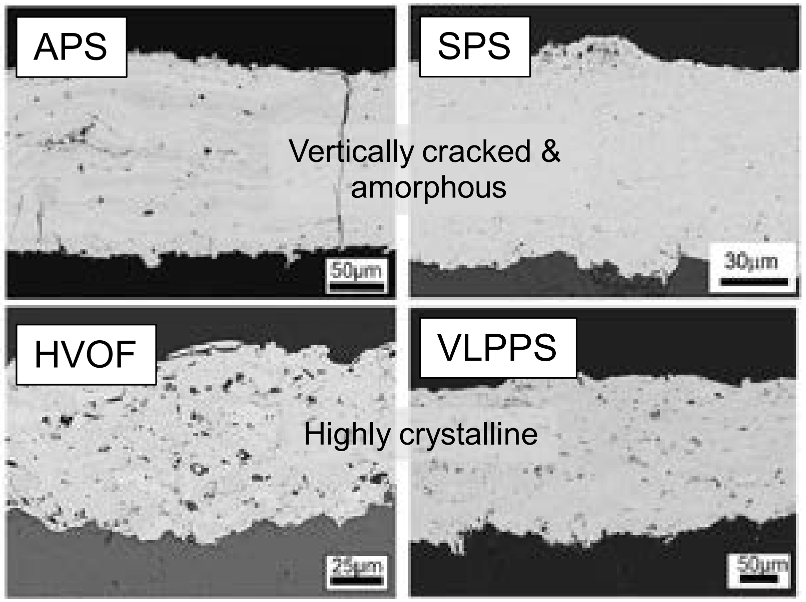


Raman Phase Maps

- **Hoher amorpher Anteil** hoch aufgrund der schnellen Abkühlung auf typischerweise niedrige Substrattemperaturen, Schrumpfung bei Hochtemperatureinsatz



APS: Atmospheric Plasma Spraying
SPS: Suspension Plasma Spraying
HVOF: High-Velocity Oxygen Fuel
VLPPS: Very Low Pressure Plasma Spraying



E.Bakan et al. J Therm Spray 26(3) 2017
E.Bakan et al. Coatings 7(4) 2017
R. Vaßen et al. Coatings 9(12) 2019

HERSTELLUNG VON EBCS FÜR TESTS

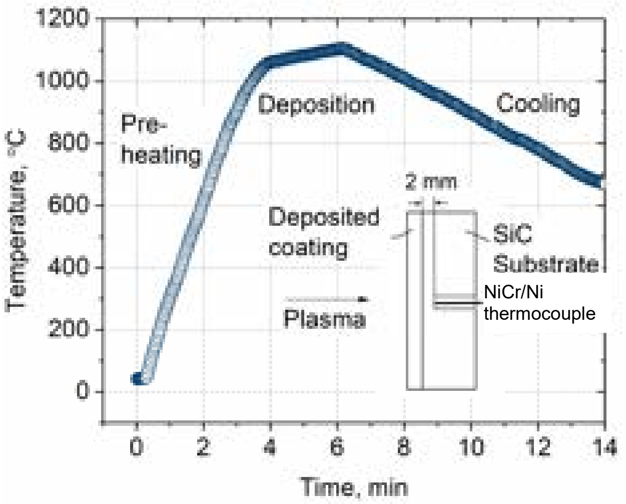
Very Low Pressure Plasma Spraying (VLPPS)

- O3CP Torch
- 110Ar/20He
- 2100A-90kW
  (Partikel-Deposition)
- 200Pa

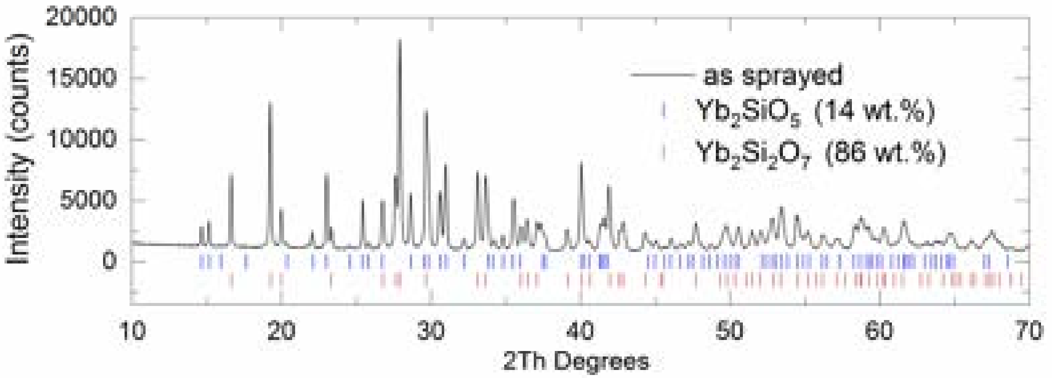
- Herstellung bei über 1000 °C
- Vor und nach Beschichtung Heizen der Probe mit Plasmafackel
- Langsame Kühlraten (~55K/min)

Kristalline und dichte Schichten!

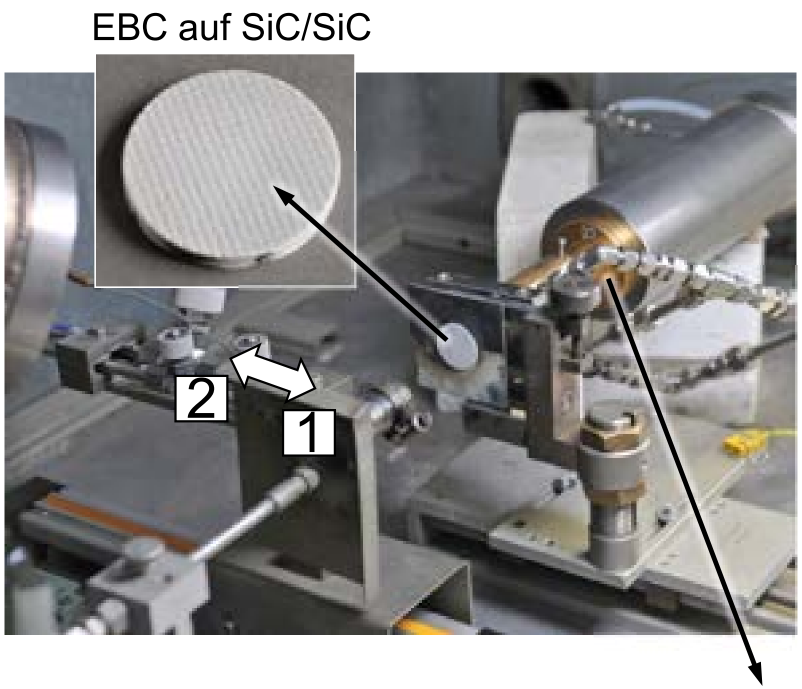
Angepasstes Temperatur-programm:



Röntgendiffraktogramm zeigt hochkristalline Schicht:



THERMISCHES ZYKLIERUNG IM GASBRENNERTEST



Angepasstes Pyrometer für die Rückseite kombiniert mit Kühldüse

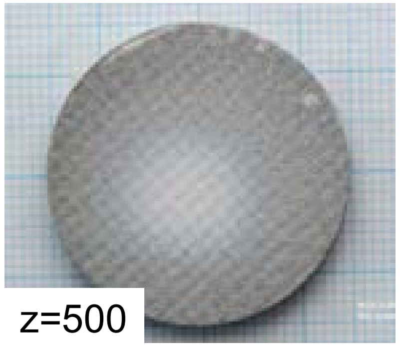
- Erdgas/Sauerstoff Brenner
- Probengröße Ø=30 mm, Dicke 3.0-3.5 mm
- 5 min Heizen, 2 min Kühlen

Bedingung	**Gesamtgasfluss [slpm]**	**Geschätzte Flammgeschwindigkeit [m/s]**	**Geschätzter Wasserdampfgehalt in Flamme(vol.%)**
Standard	1146	8	49
Mit H_2O Injektion (120 g/h)	1611	47	53

Probe	**Test-Bedingungen**				
	Waserinjektion	Aufprall-winkel	$T_{Oberfläche}$	$T_{Rückseite}$	Zyklen-anzahl
1	Nein (Standard)	90°	1250 °C	650 °C	500
2	Ja	90°			
3	Ja	45°			

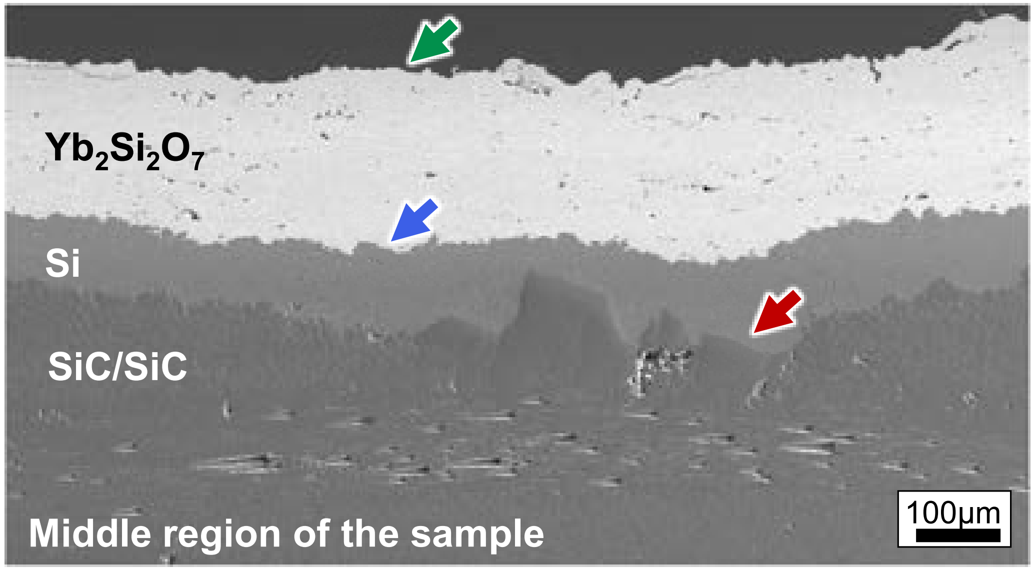
E.Bakan et al. J. Europ. Ceram. Soc 40 (2020) 6236

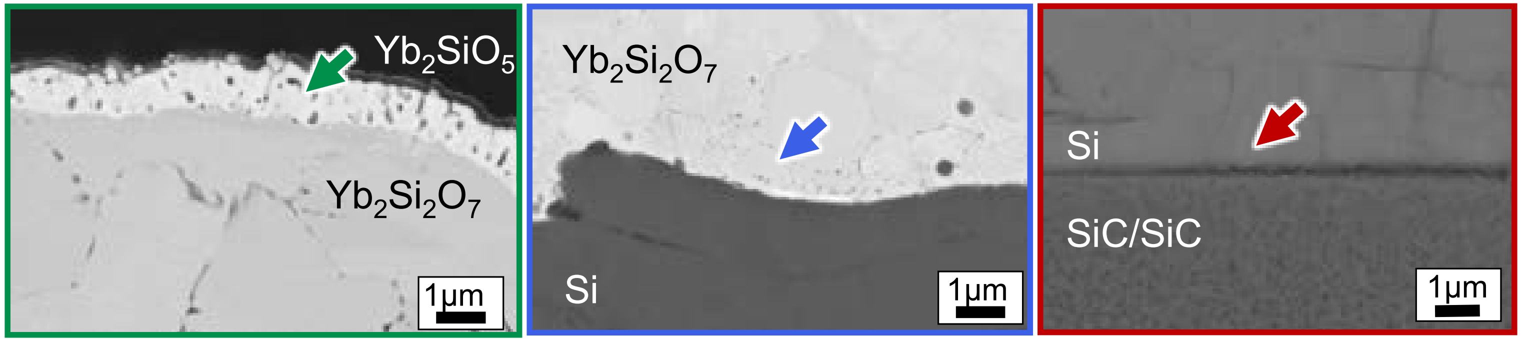
BURNER RIG TEST (STANDARD) RESULTS



Test conditions:
$T_{surface}$=1250 °C,
T_{back}=650 °C,
$T_{bond\ coat}$= 1120 °C

(approx. 42 h high temperature hold, 17 h cooling periods)





I. **Indications of $Yb_2Si_2O_7$ reaction with H_2O (g) produced by the natural gas combustion**

II. No visible oxidation product at the Si & SiC/SiC interfaces

III. The concentrated corrosion in the central part is probably associated with higher temperature in this region

BURNER RIG TEST (+H_2O liq.) RESULTS

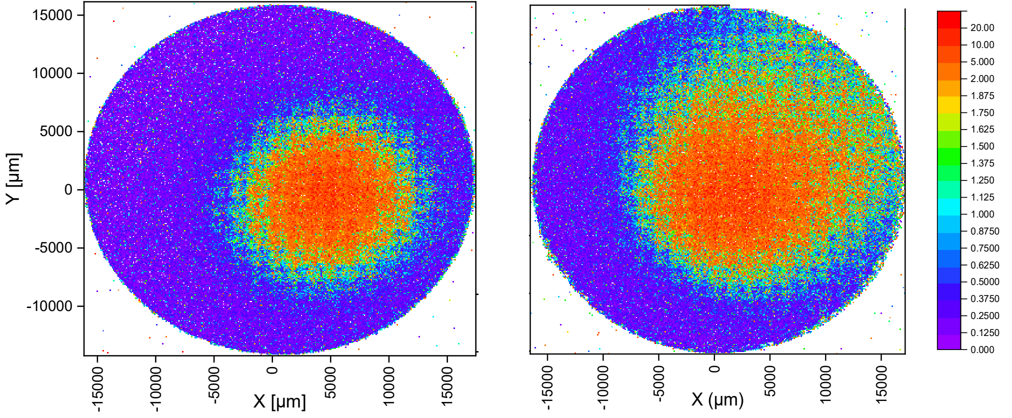
90° test
120g/h H_2O injection

45° test
120g/h H_2O injection

Test conditions:

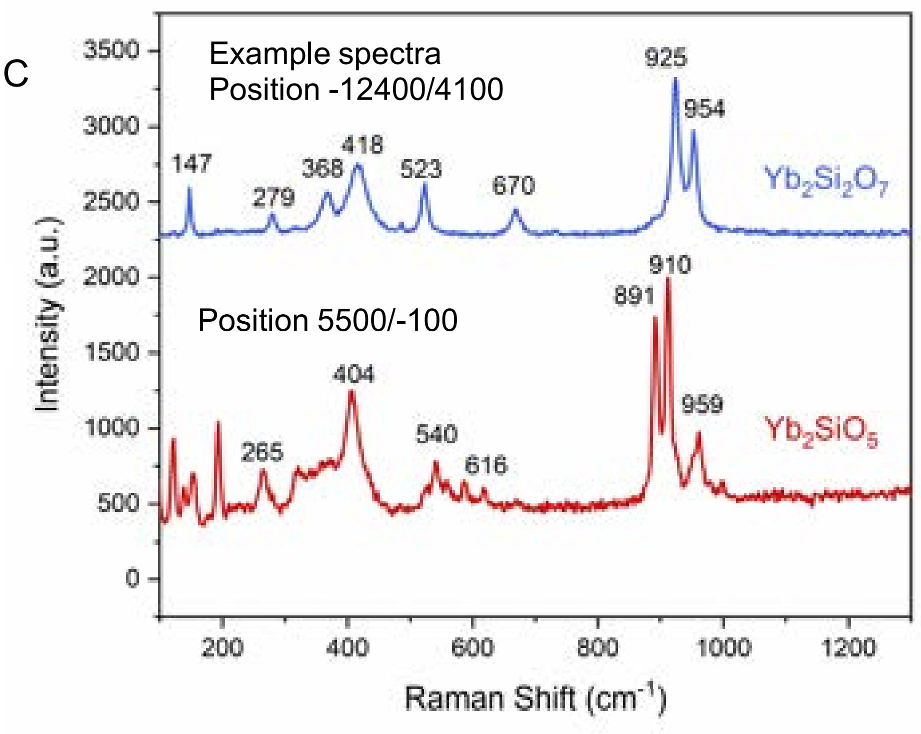
$T_{surface}$=1250 °C
T_{back}=650 °C
$T_{bond\ coat}$= 1120 °C
500 cycles

Peak Intensity
Yb_2SiO_5 910/ $Yb_2Si_2O_7$ 925



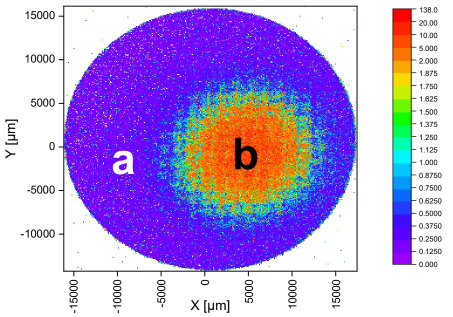
Raman
phase
maps

Measurement conditions:
Laser: 532 nm
Integration time: 0.2 s
Number of spectra: over 100000
Step size of mapping: 100 µm

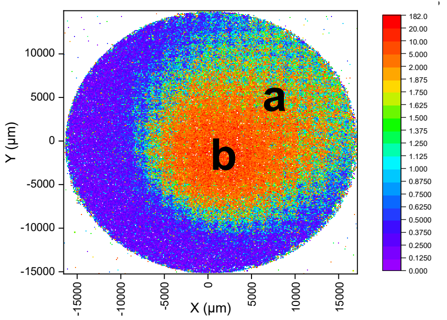


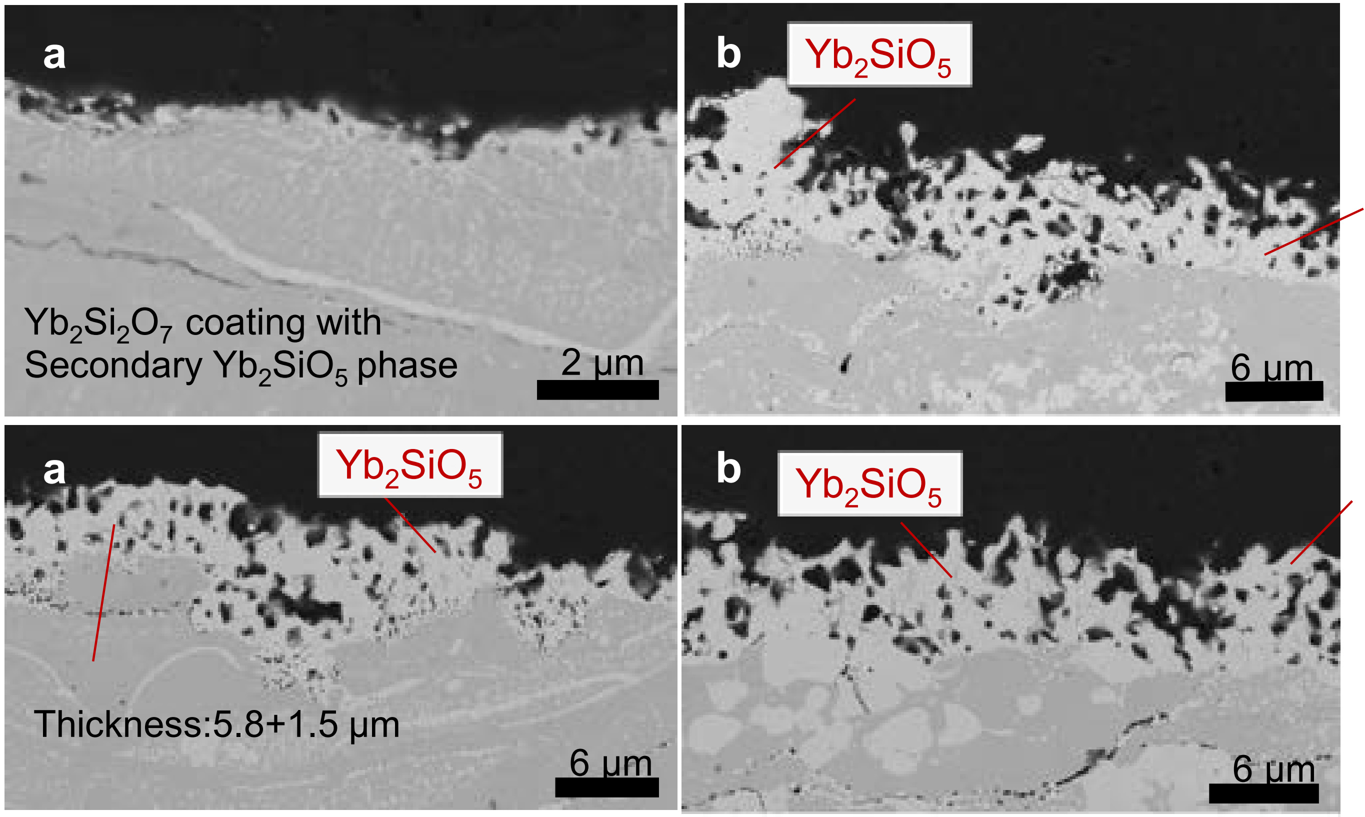
BURNER RIG TEST (+H_2O liq.) RESULTS

90° test
120g/h H_2O injection



45° test
120g/h H_2O injection





Thickness:
5.7+1.8µm

Thickness:
7.3+0.7µm

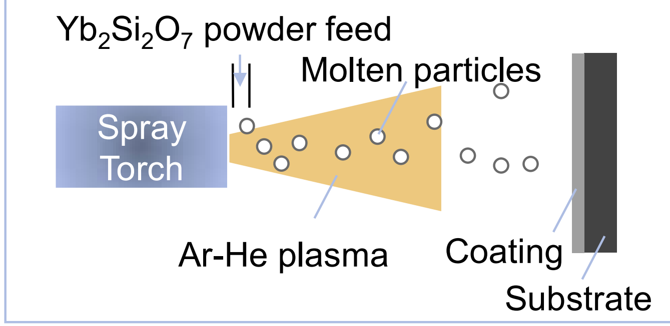
- T_{surf}=1250 °C, 500 cycles approx. 42 h high temperature hold, 17 h cooling periods

VR1

HIGH VELOCITY STEAM CORROSION TEST OF APS EBCS

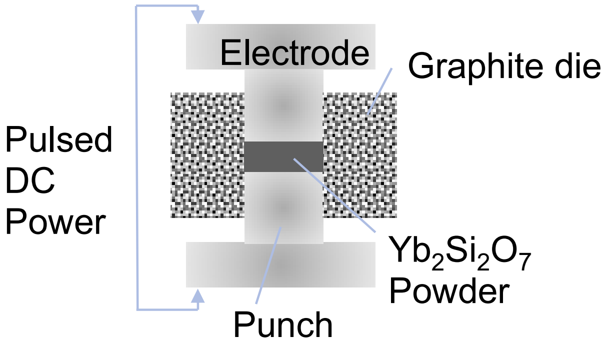
Sample Preparation

Atmospheric Plasma Spraying (APS)



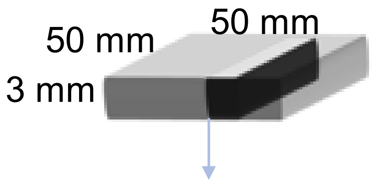
Ar/He:
46/4slpm
520 A

Field Assisted Sintering Technology-Spark Plasma Sintering (FAST-SPS)



1650 °C
50 MPa
100K/min

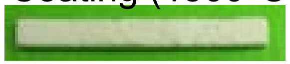
Free-standing coating and sintered powder sample were cut into bars



3.0 x 3.8 x 36 mm

As-sprayed coating (amorphous)

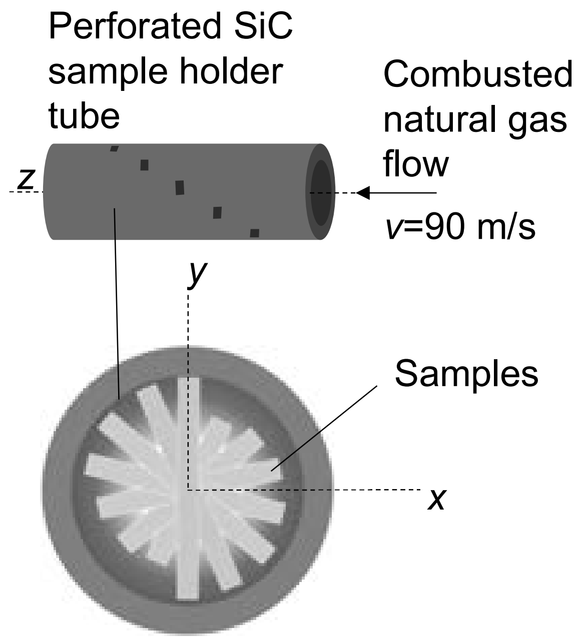
Coating (1500°C-40 h, air)



FAST-SPS

Test Conditions

T=1400 °C, P_{H2O}=0.19 atm, P_{total}=1 atm

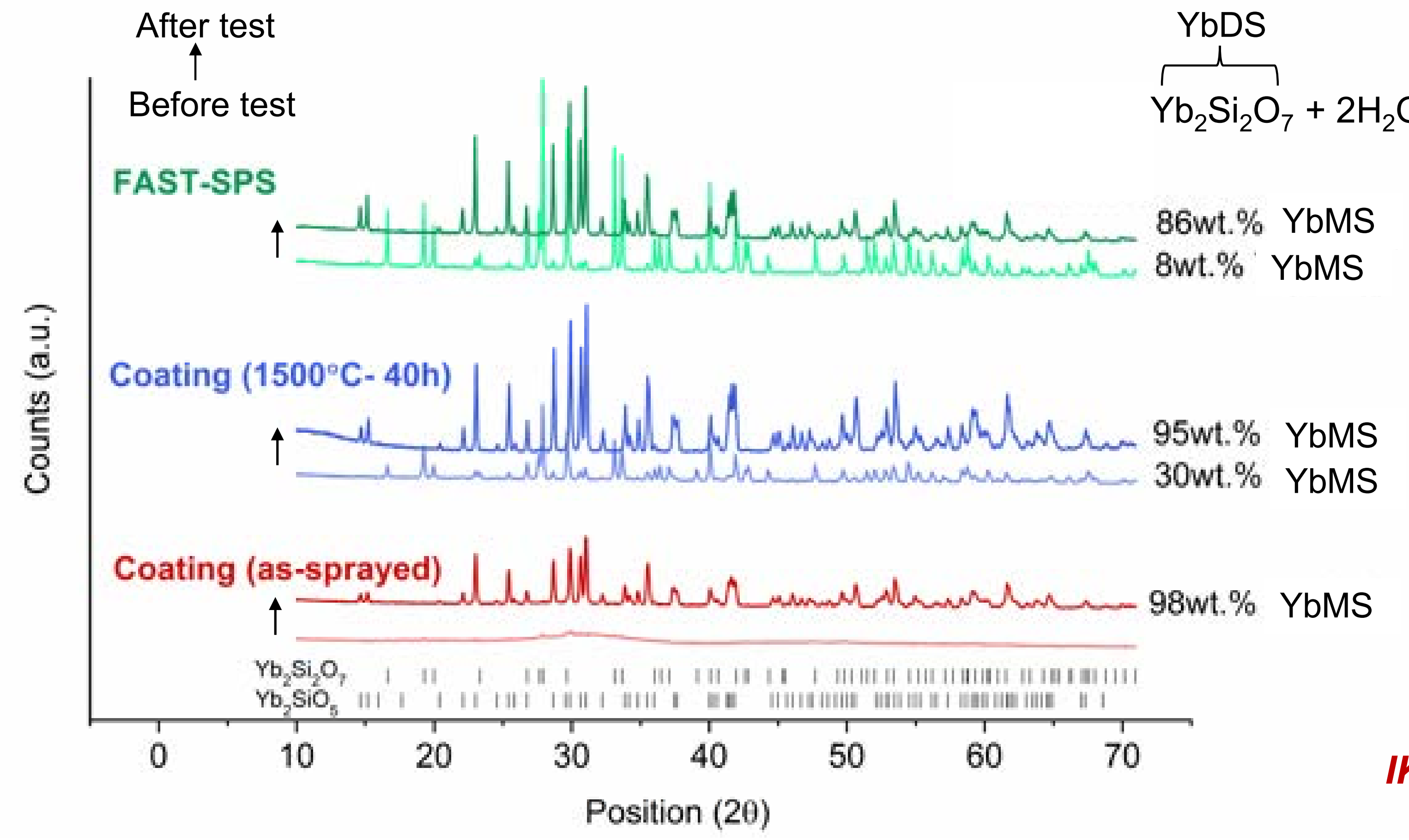


IKTS Dresden, Dr. Hagen Klemm

Folie 13

VR1 Vaßen, Robert; 31.03.2022

PHASE COMPOSITION OF SAMPLES BEFORE AND AFTER TEST



$$\overbrace{Yb_2Si_2O_7}^{\text{YbDS}} + 2H_2O(g) = Si(OH)_4(g) + \overbrace{Yb_2SiO_5}^{\text{YbMS}}$$

After test, surface depletion of SiO_2 from YbDS to form YbMS

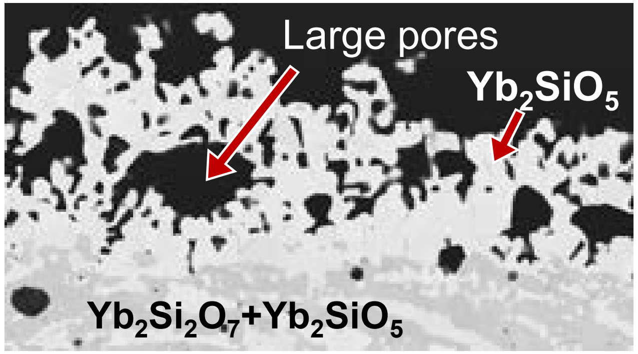
Si evaporation during plasma spraying of **YbDS feedstock (5 wt.% YbMS)**

As-sprayed coating is almost fully amorphous before the test, recrystallization takes place during the test

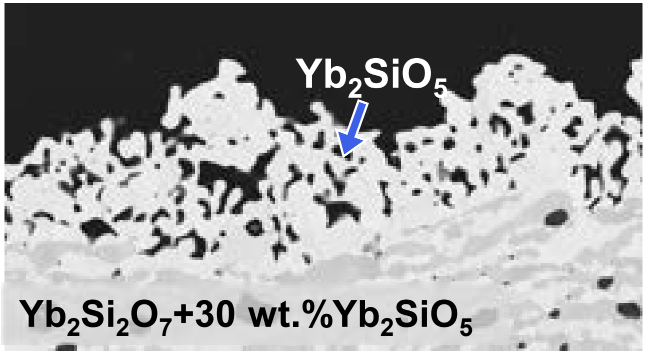
IKTS Dresden, Dr. Hagen Klemm

MICROSTRUCTURE OF SAMPLES AFTER TEST

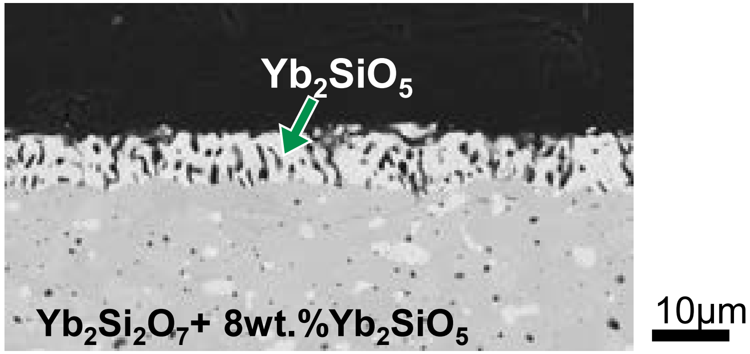
Coating (as-sprayed)



Coating (1500 °C-40 h, air)

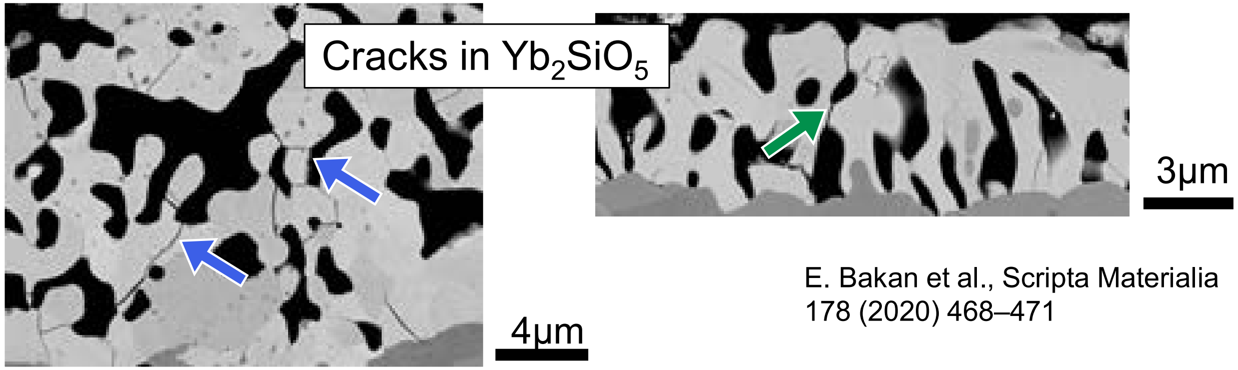


FAST-SPS



$Yb_2Si_2O_7$ + $2H_2O$ (g) = $Si(OH)_4$ (g) + Yb_2SiO_5 + porosity

Different pore morphology in Yb_2SiO_5 scales of coatings vs. FAST SPS

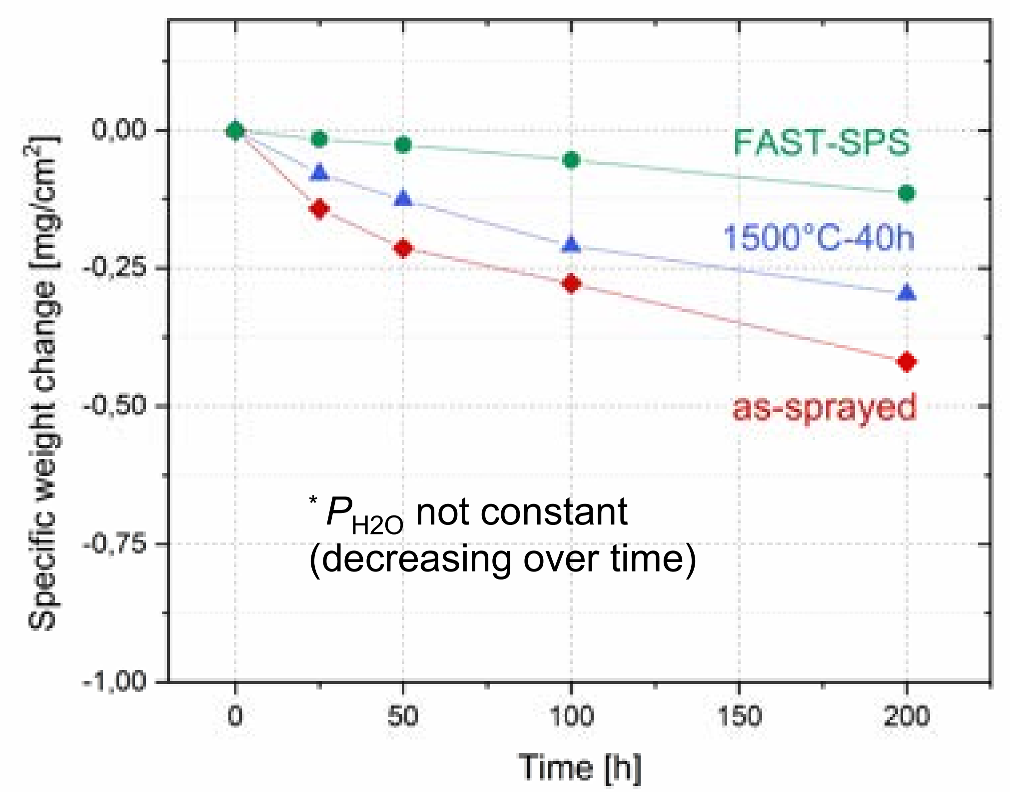


E. Bakan et al., Scripta Materialia 178 (2020) 468–471

IKTS Dresden, Dr. Hagen Klemm

HIGH VELOCITY STEAM CORROSION TEST RESULTS

Test conditions:
T=1400 °C, v=90 m/s, P_{H2O}=0.19 atm*, P_{total}=1 atm



* P_{H2O} not constant (decreasing over time)

- Yb-silicate samples show reducing weight loss (k) as a function of time

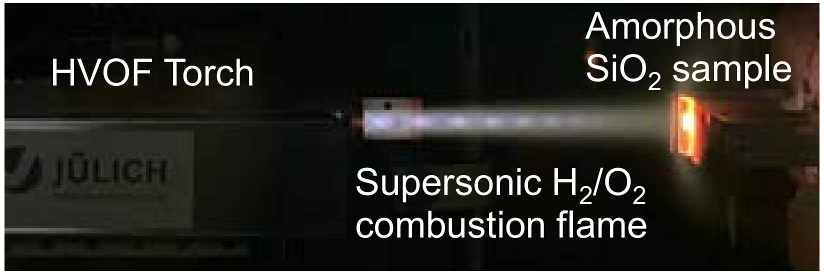
  $k_{\text{as-sprayed}} > k_{1500°C\text{-}40h} > k_{\text{FAST-SPS}}$

- **Parabolic weight loss kinetic** of $Yb_2Si_2O_7$ was also shown in an earlier work at similar and constant test conditions
  (PhD thesis, M. Fritsch, IKTS,, Dresden)

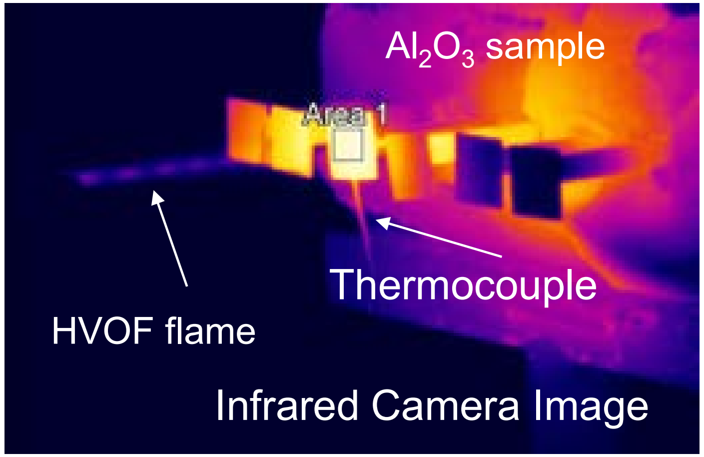
- Possible diffusion limited process

IKTS Dresden, Dr. Hagen Klemm

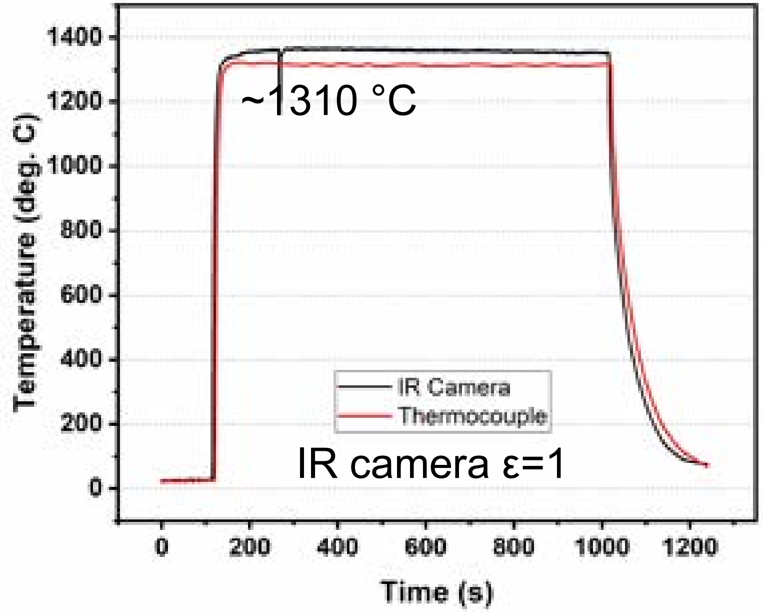
HVOF TEST CONDITIONS (DJ 2600, OERLIKON)



460 slpm shroud gas (air)
275 slpm O_2
550 slpm H_2
150 mm SOD



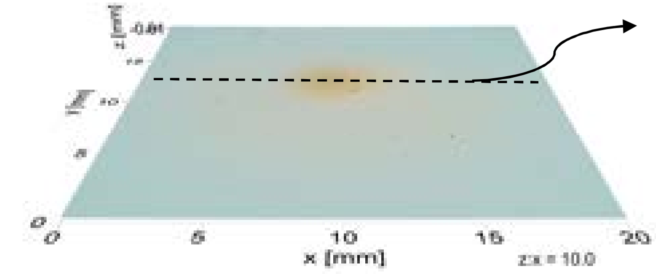
Infrared Camera Image



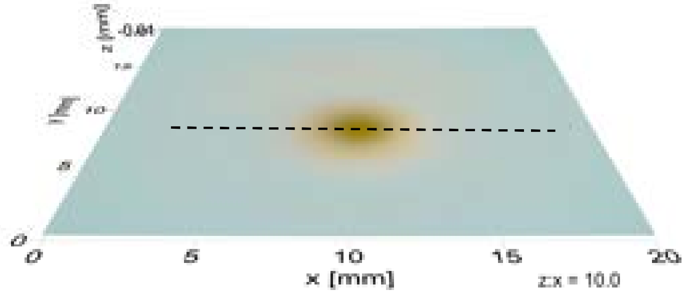
~1310 °C

IR camera ε=1

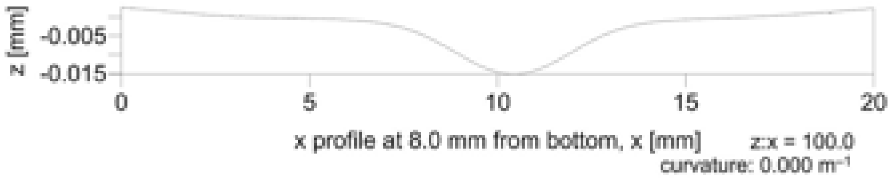
HVOF TEST-SiO_2

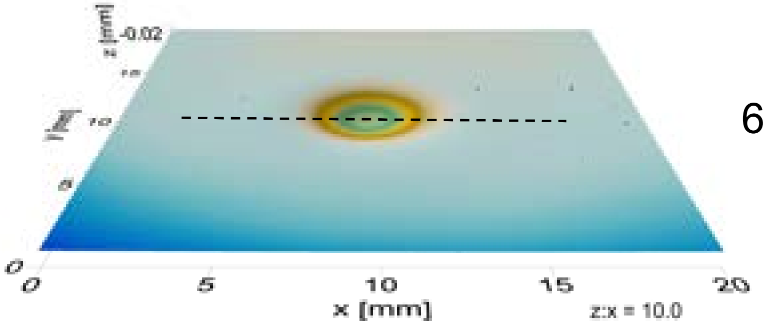


15 min



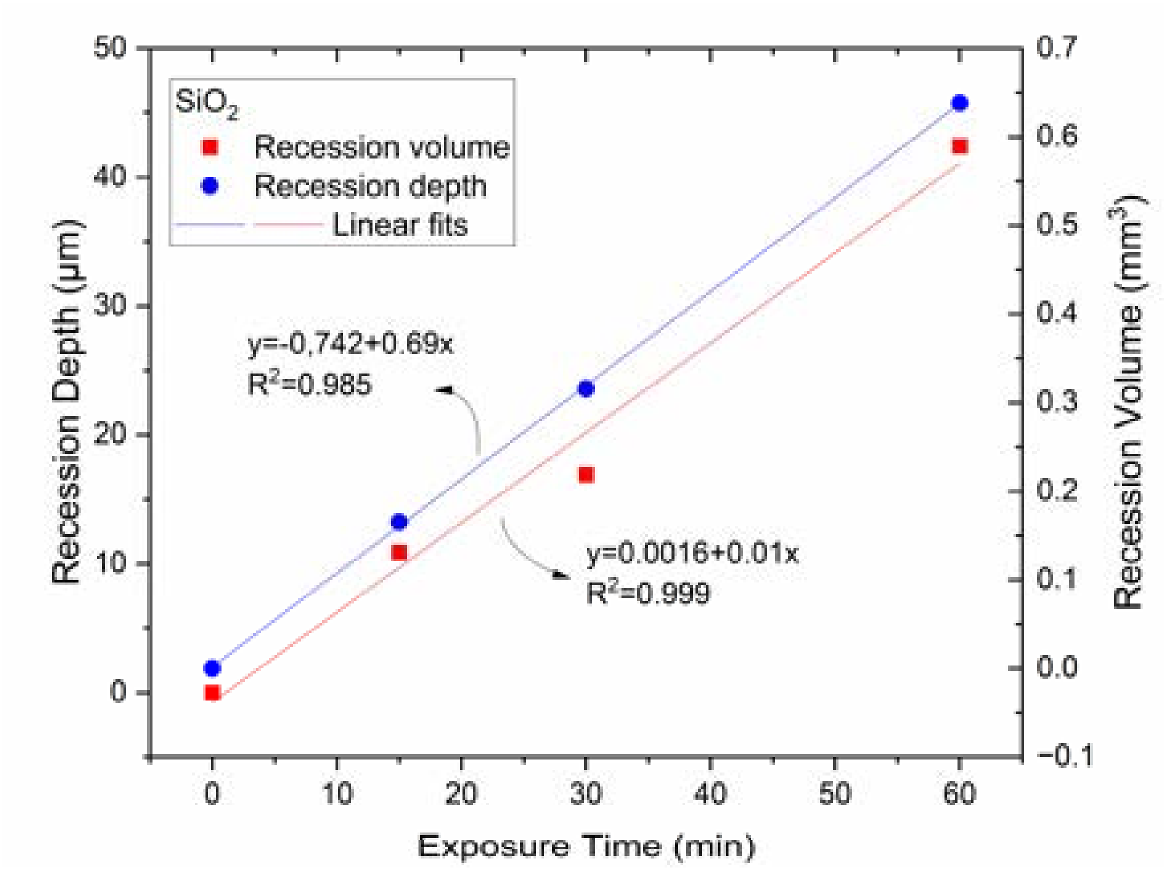
30 min





60 min

RECESSION RATE –SiO_2



$SiO_2 + 2H_2O\ (g) \rightarrow Si(OH)_4\ (g)$

- **41 µm/h, 0.6 mm^3/h recession rate**
- Linear volatilization kinetics

RECESSION RATE – SiO_2 – 1300 °C

Gas-boundary layer theory

$$J_l = 0.664\left(\frac{\rho v L}{\mu}\right)^{1/2}\left(\frac{\mu}{\rho D_{AB}}\right)^{1/3}\frac{D_{AB}\rho'}{L}$$

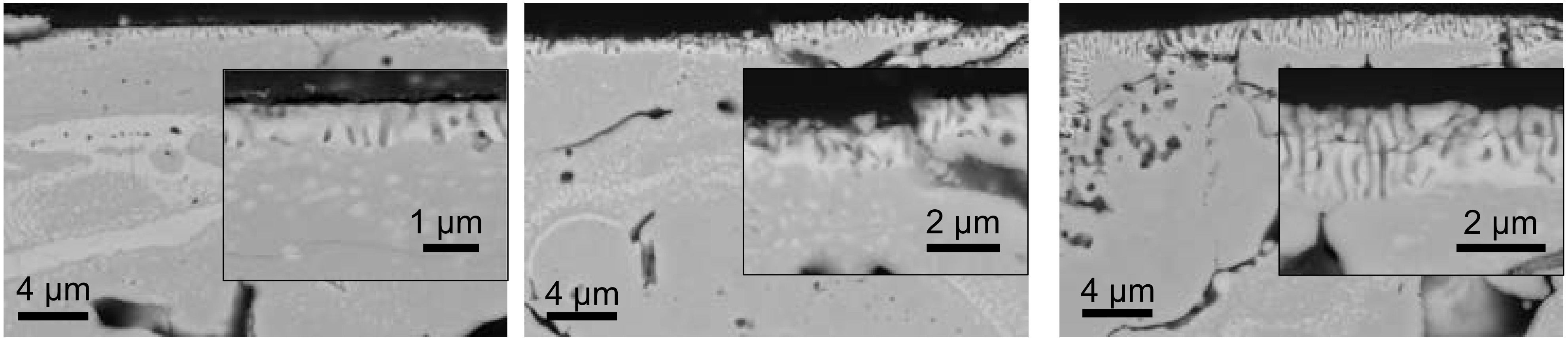
$$J_t = 0.0365\left(\frac{\rho v L}{\mu}\right)^{0.8}\left(\frac{\mu}{\rho D_{AB}}\right)^{1/3}\frac{D_{AB}\rho'}{L}$$

The model (with the assumption of 0.5atm H_2O pressure) estimates x6 larger recession rate in HVOF test (turbulent conditions) vs. Golden & Opila.
Calculated recession rate is roughly half of the experimentally observed value.

		Golden & Opila J. Eur. Ceram. Soc. (36) 1135-1147, 2016	**HVOF Test** This study
$\rho(T)$, g/cm^3	The concentration of H_2O in the boundary layer, ideal gas law	1,40E-04 (1 atm)	6,98E-05 (0.5 atm)
v, cm/s	Gas velocity	1,72E+04	2,24E+05 (*)
L , cm	Length of specimen exposure	7,50E-01	5,00E-01
$\mu(T)$, g/cms	Gas viscosity	5,44E-04	5,44E-04
$D_{AB}(T)$, cm^2/s	The interdiffusion coefficient for the volatile species in the gas boundary layer	2,41E+00	2,41E+00
ρ`(T), g/cm^3	Equilibrium concentration of the volatile species at the oxide–gas interface, ideal gas law	3,70E-09	3,70E-09
J_l, g/cm^2s	Mass flux, laminar	5,33379E-07	2,0992E-06
J_t, g/cm^2s	Mass flux, turbulent	3,33808E-07	2,0391E-06
R_{max-l}, µm/h	Calculated recession depth, laminar	5,17E+00	2,04E+01
R_{max-t}, µm/h	Calculated recession depth, turbulent	3,23E+00	1,98E+01

(*) Gatzen et al., J Am Ceram Soc. 2019;102:6850–6862.

HVOF TEST- APS YbDS POLISHED

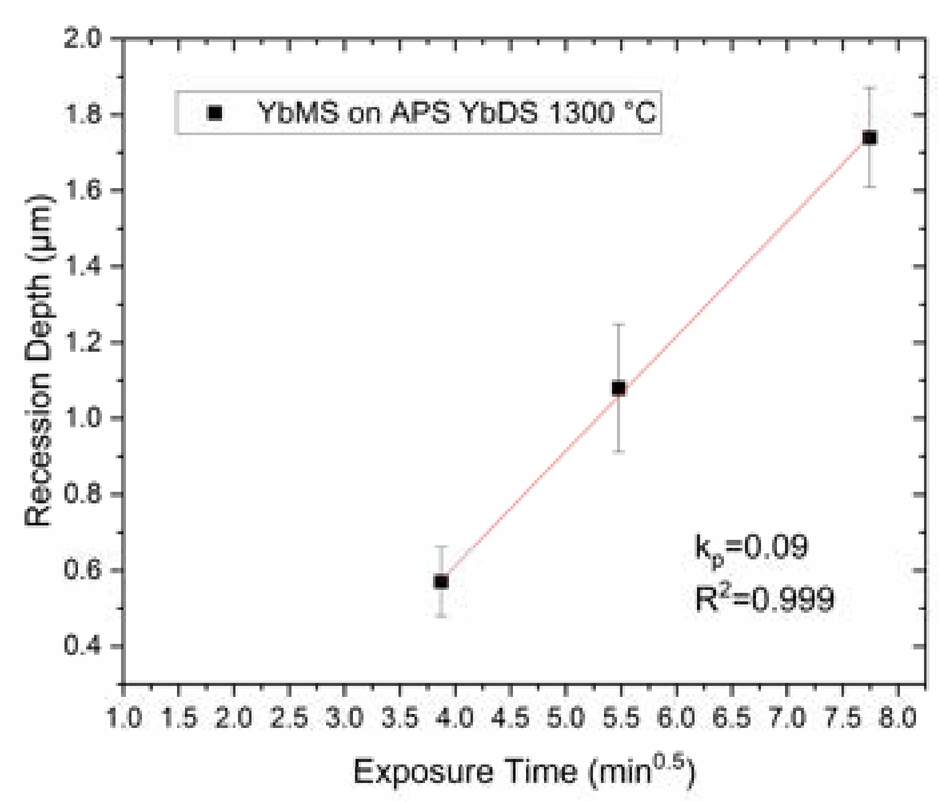

15 min

30 min

60 min

Central part of the samples

HVOF TEST- APS YbDS POLISHED



- **Parabolic reaction kinetics**, possibly diffusion-controlled
- In contrast to SiO_2 results, **kinetics for YbDS reaction is slower** (0.09 $µm^2$/min or 5.47 $µm^2$/h) in HVOF test in comparison with the literature:

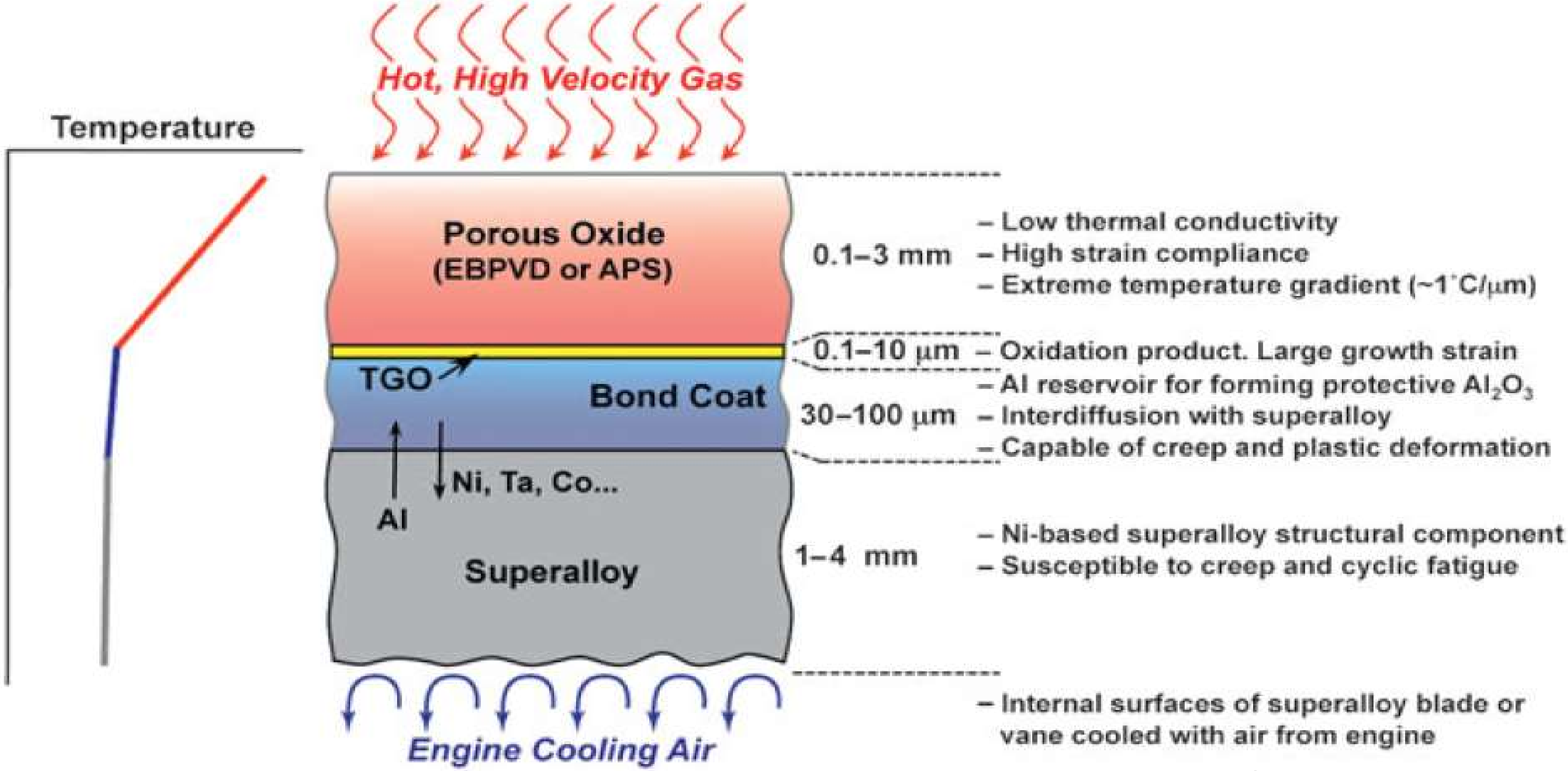
k_p=7±1 $µm^2$/h at 80-115 m/s, 1300°C, 1 atm H_2O

M. Ridley and E. Opila, Journal of the European Ceramic Society 41 (2021) 3141–3149

Possible reasons:

Error in the measurement?
Inadequate theoretical description!

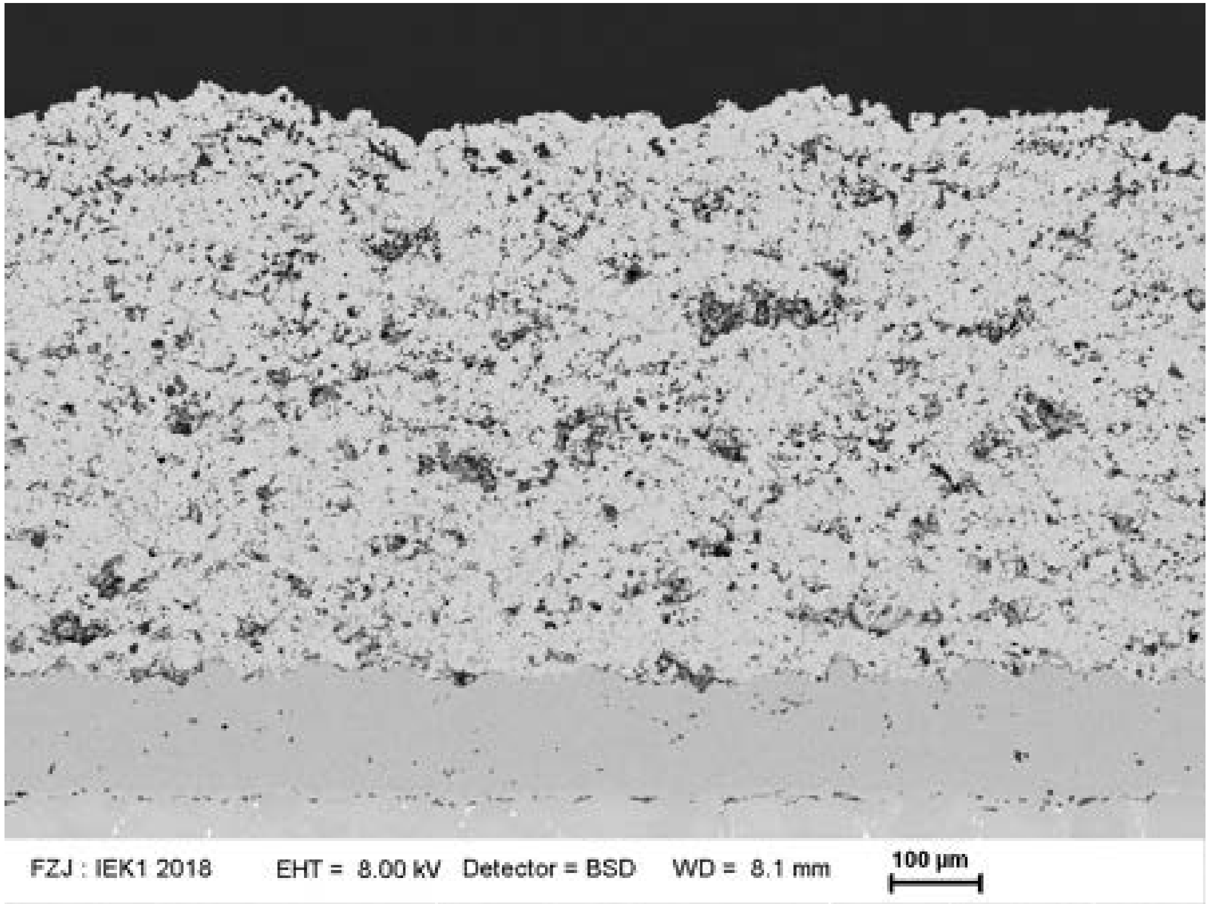
Principle of Thermal Barrier Coatings (TBCs):



MRS Bulletin 2012 Vol . 37 No. 10

stationary condition: $j_Q = -\lambda \frac{\Delta T}{\Delta x}$

APS WÄRMEDÄMMSCHICHTSYSTEM



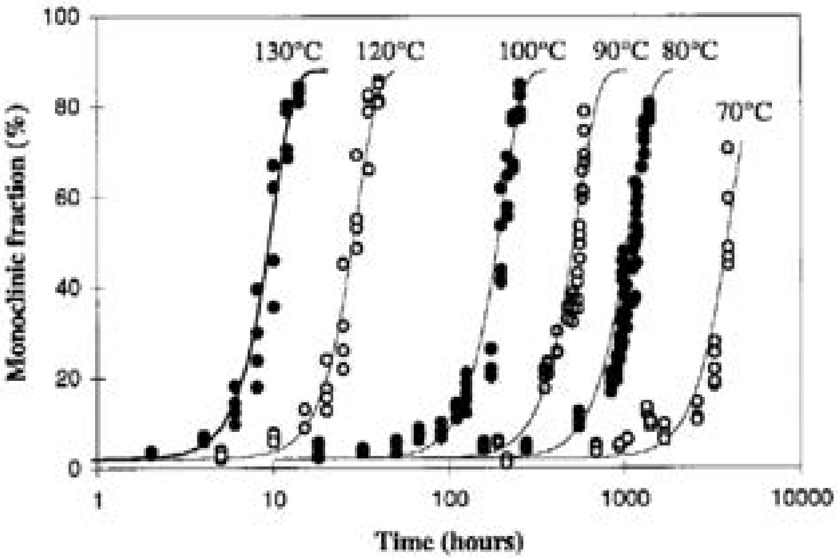
7YSZ Amperit Pulver
(H.C. Starck Amperit 827.006,
d_{10}=54 µm, d_{50}=80 µm, d_{90}=112 µm)
TriplexPro Brenner,
15% Porosität

NiCoCrAlY (Oerlikon Metco, Amdry 386) VPS F4 Haftvermittlerschicht

IN738 Substrate

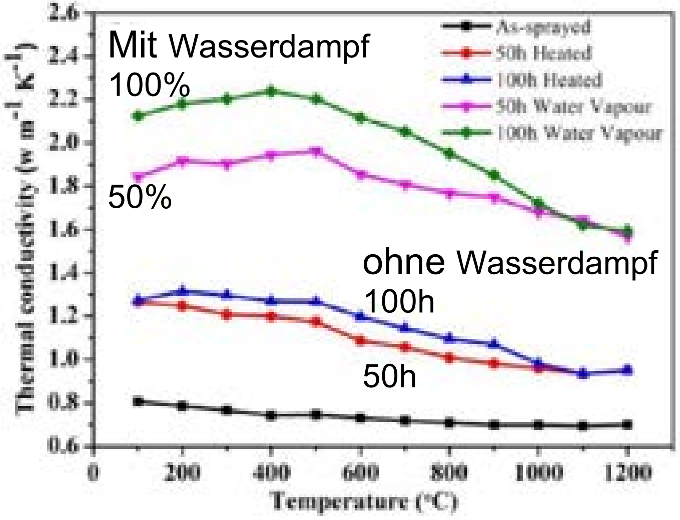
EINFLUSS VON WASSERDAMPF AUF APS SYSTEME

Phasenumwandlung in 3 YSZ



Chevalier et al 2005

Sintern bei 1100°C



Mit Wasserdampf
100%

50%

ohne Wasserdampf
100h

50h

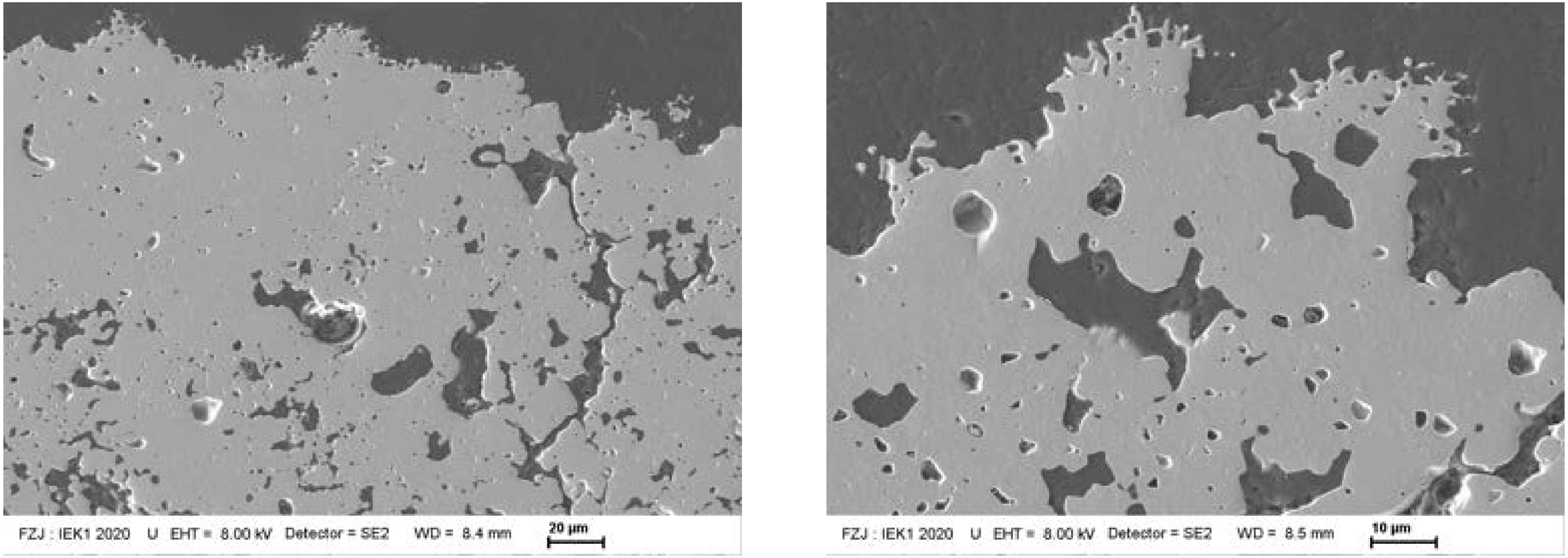
Sivakumar et al 2018

Wasserdampf hat Einfluss auf Phasenumwandlung und Sintern

Neue Projekte sind angelaufen, Zusammenhänge genauer zu klären

REM Mikrostrukturabbildung von Gasbrenner-Probe

Langsame Abkühlung ($T_{\text{Oberfläche}}$ = 1554°C, T_{Bondcoat} = 1088°C, Zyklen beim Versagen 1933 (~160 h).



Facettierte Oberflächenbereiche

Gasphasenreaktion von YSZ mit Brennergasströmung (H_2O?)

Zusammenfassung

Standard EBC Schichten ($Yb_2Si_2O_7$) zeigen deutliche Degradation unter schnellem Wasserdampf

Die Degradationsraten werden stark von der Geschwindigkeit, der Porosität und der Temperatur bestimmt

Unterschiedliche Testmöglichkeiten wurden vorgestellt (Gasbrenner, IKTS Rig, HVOF Brenner, Ofen), die genauen Randbedingungen bestimmen die Ergebnisse

Auch Wärmedämmschichten (YSZ) zeigen eine Degradation (Sintern, Phasenumwandlung, Abdampfen?) unter Wasserdampf, genaue Analysen ausstehend

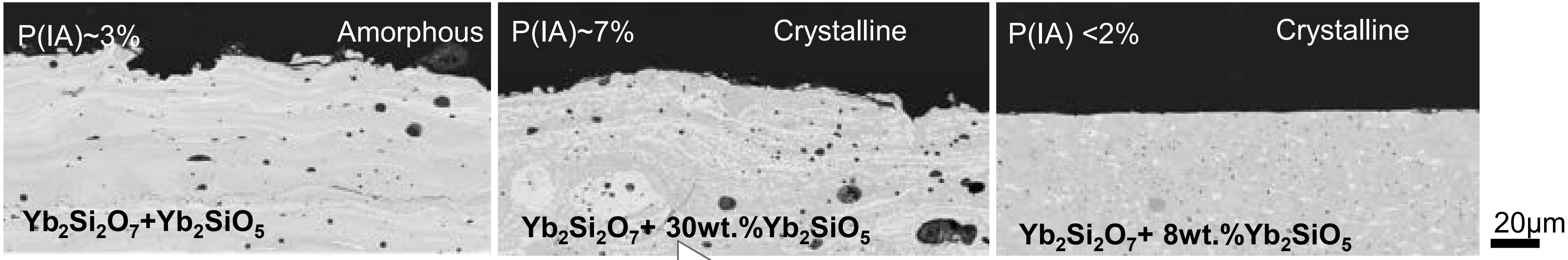
Danke für Ihre Aufmerksamkeit!

MICROSTRUCTURE OF THE SAMPLES BEFORE TEST

Coating (as-sprayed)

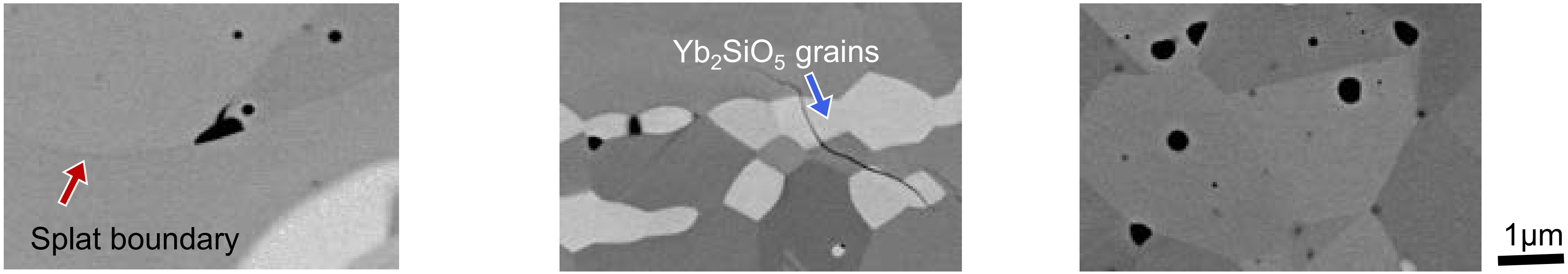
Coating (1500 °C-40 h)

FAST-SPS



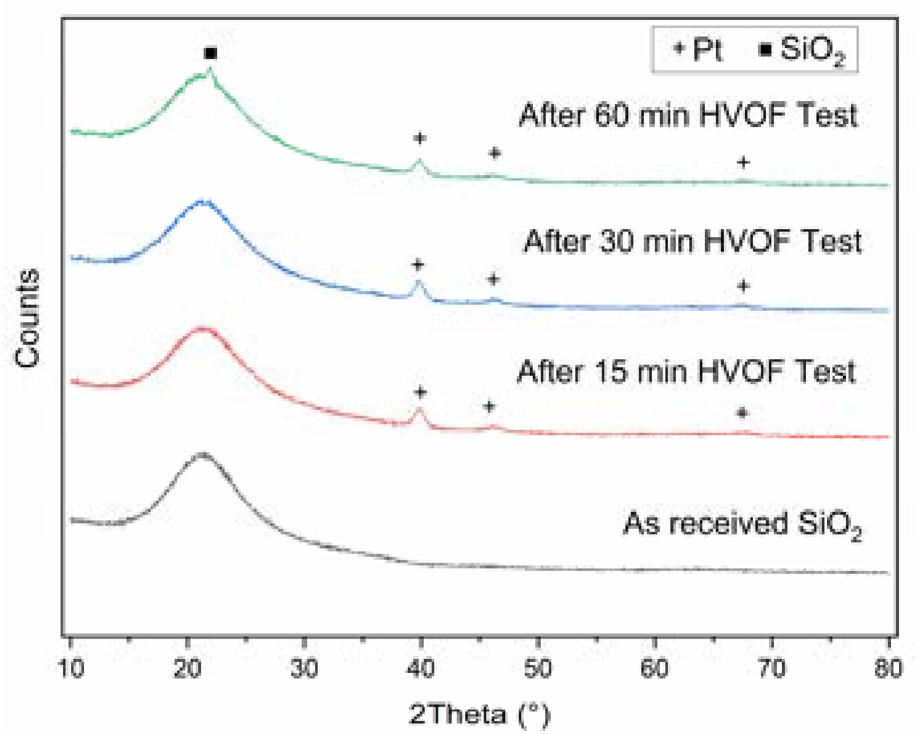
Porosity increases due to crystallization shrinkage

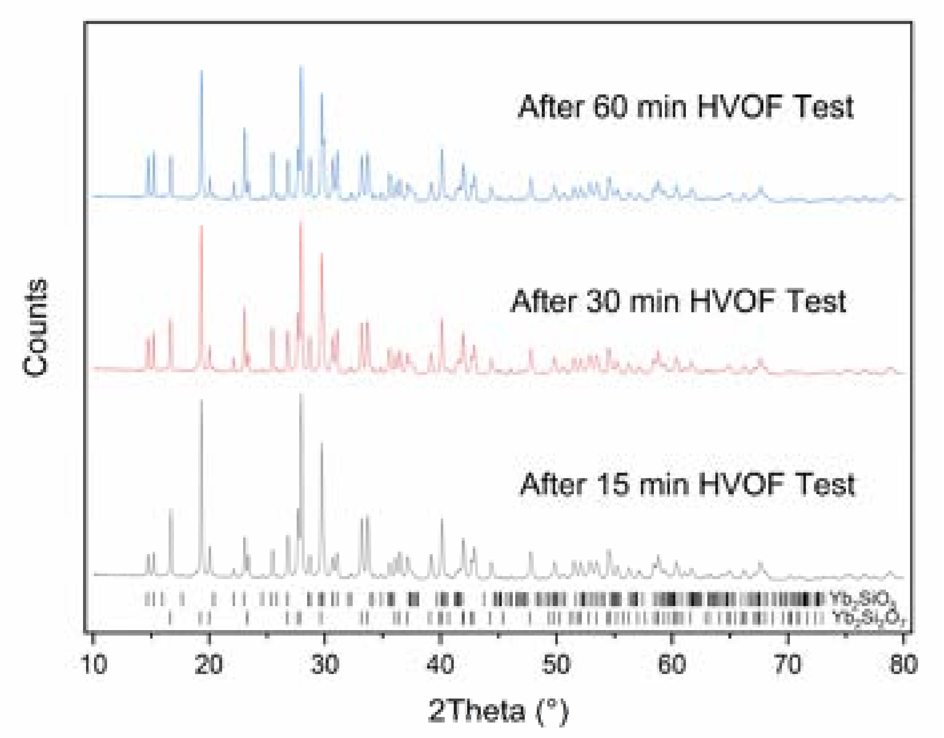
More homogenous pore distribution and smaller pores



Grain size changes from ~1-2 µm to 5-6 µm

XRD

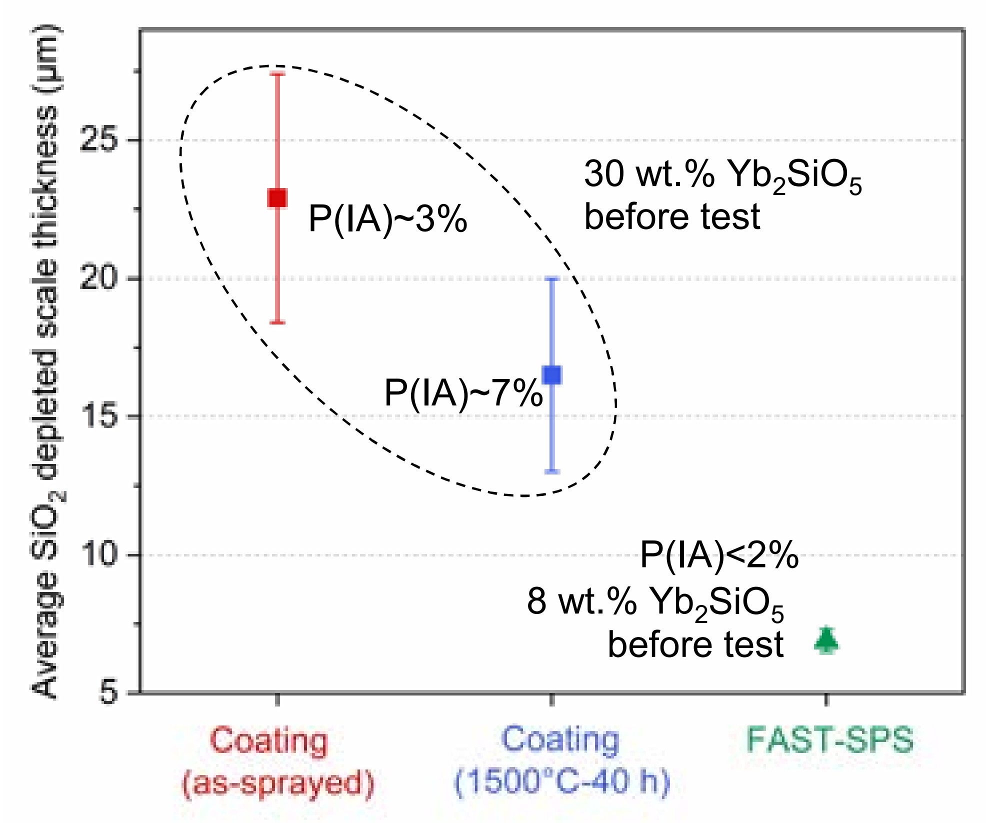




- Indication of crystallization (cristobalite SiO2) after 1 h testing
- Pt layer was added to make the surface reflective to light for surface profilometry measurements

- YbMS content increase is also visible at longer test times via XRD

HIGH VELOCITY STEAM CORROSION TEST RESULTS



P(IA)~3%

P(IA)~7%

30 wt.% Yb_2SiO_5 before test

P(IA)<2%

8 wt.% Yb_2SiO_5 before test

- SiO_2 depleted scale thicknesses (*t*) consistent with the measured weight losses (*k*)

$$k_{\text{as-sprayed}} > k_{1500°\text{C-40h}} > k_{\text{FAST-SPS}}$$

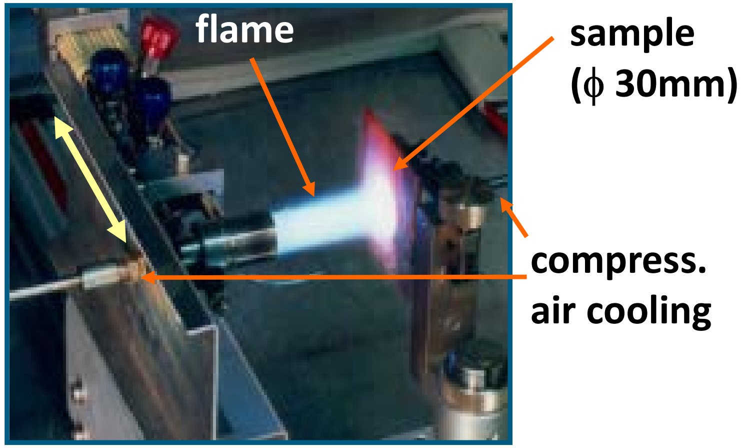
$$t_{\text{as-sprayed}} > t_{1500°\text{C-40h}} > t_{\text{FAST-SPS}}$$

- Higher volume of porosity possibly increases the inward H_2O (g)/outward $Si(OH)_4$ (g) diffusion rates in the coatings vs. FAST-SPS sample

- Differences between as-sprayed and 1500 °C-40 h coating possibly related to recrystallization (=large pores in Yb_2SiO_5 scale) in the as-sprayed coating

Burner rig testing

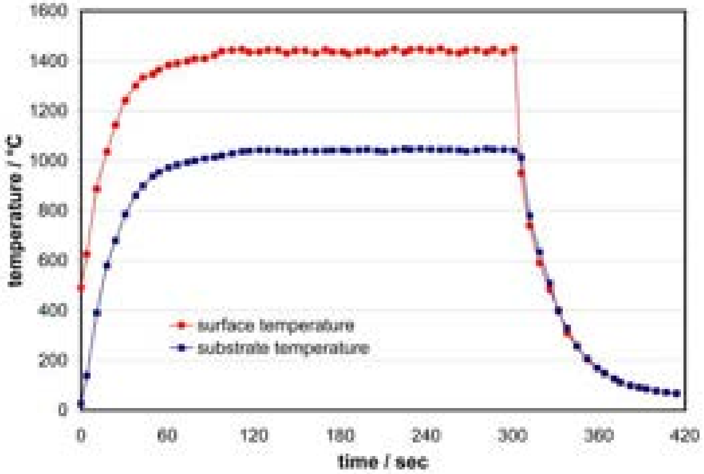
- 7 rigs available operated with CH_4/oxygen burners & compressed air cooling
- Independent adjustment and control of surface (measured with pyrometer)
  & substrate temperatures (thermocouple in substrate)
- High cyclic loading in combination with TGO growth



Typical test conditions:

- $T_{substrate}$ 1050°C
- $T_{interface}$ ~1090°C
- $T_{surface}$ 1400°C
- Cycle duration:

  5 min heating, 2 min cooling



ENVIRONMENTAL BARRIER COATINGS (EBCS)

Protection of Ceramic Matrix Composites (CMCs)

SiC/SiC CMC

Ox/Ox CMC
(Al_2O_3/ Al_2O_3)

Structural materials for gas turbine engine components along the hot gas path

Volatilization in water vapor

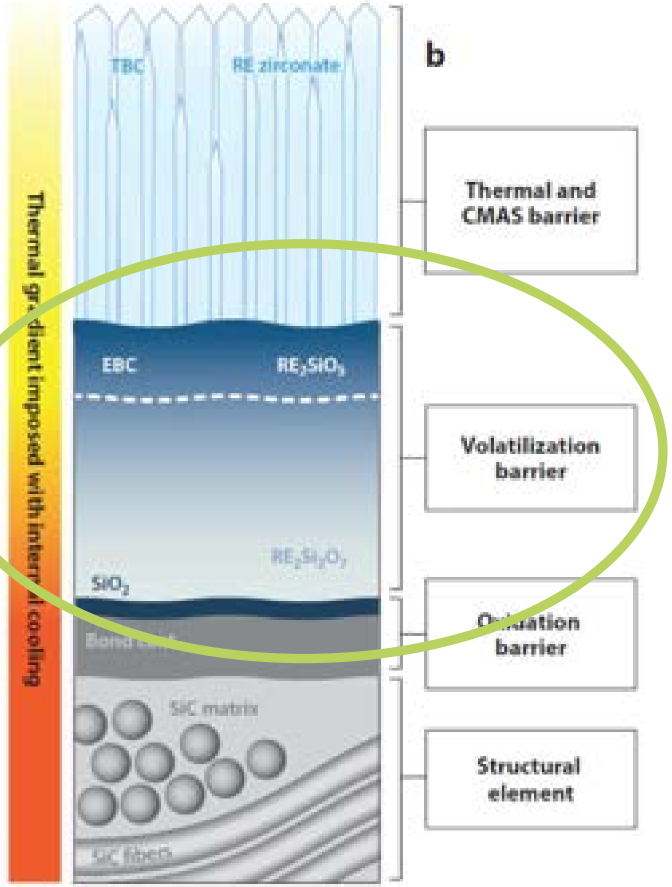
$$\mathbf{SiC(s)} + 3H_2O(g) \rightarrow \mathbf{SiO_2(s)} + 3H_2(g) + CO(g)$$

$$\mathbf{SiO_2(s)} + 2H_2O(g) \rightarrow \mathbf{Si(OH)_4(g)}$$

$$k_{laminar} = a.\exp\left(\frac{-E}{RT}\right).v^{1/2}.(P_{H_2O})^n.P^{-1/2}$$

$$k_{turbulent} = a.\exp\left(\frac{-E}{RT}\right).v^{4/5}.(P_{H_2O})^n.P^{-1/5}$$

E. J. Opila et al., J. Am. Ceram. Soc., 1999

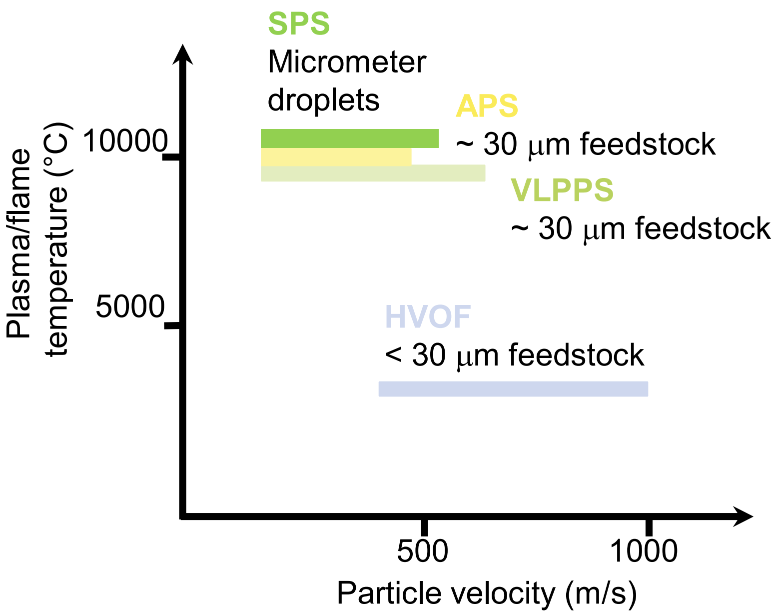


D. L. Poerschke et al., Annu. Rev. Mater. Res. 47 (2017) 297-330

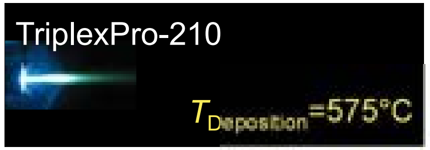
THERMAL SPRAY TECHNIQUES: APS, SPS, HVOF & VLPPS

APS	Atmospheric Plasma Spraying
SPS	Suspension Plasma Spraying
HVOF	High Velocity Oxygen Fuel Spraying
VLPPS	Very Low Pressure Plasma Spraying

Deposition Conditions and Feedstock



$184Ar/37H_2/25N_2$
3*220A
70mm

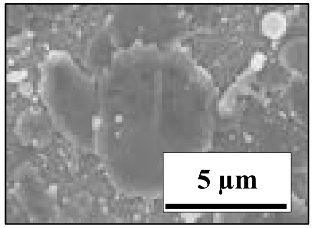


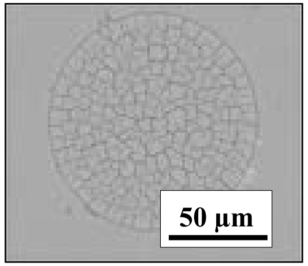
$46Ar/4H_2$
520A
90mm

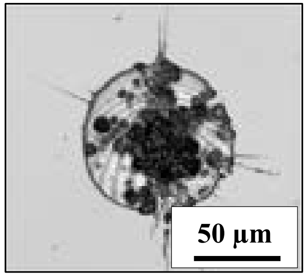
110Ar/20He
2100A
700mm

Oxygen/
methane
395/190
325mm

Typical splats:

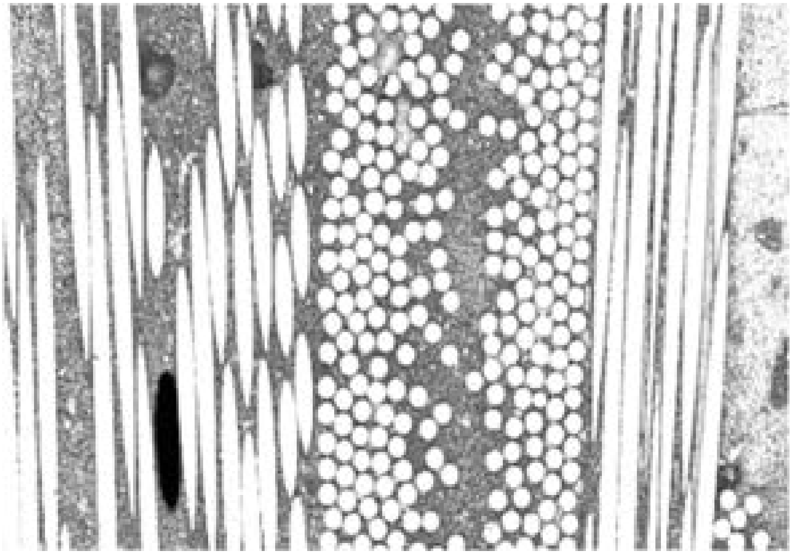






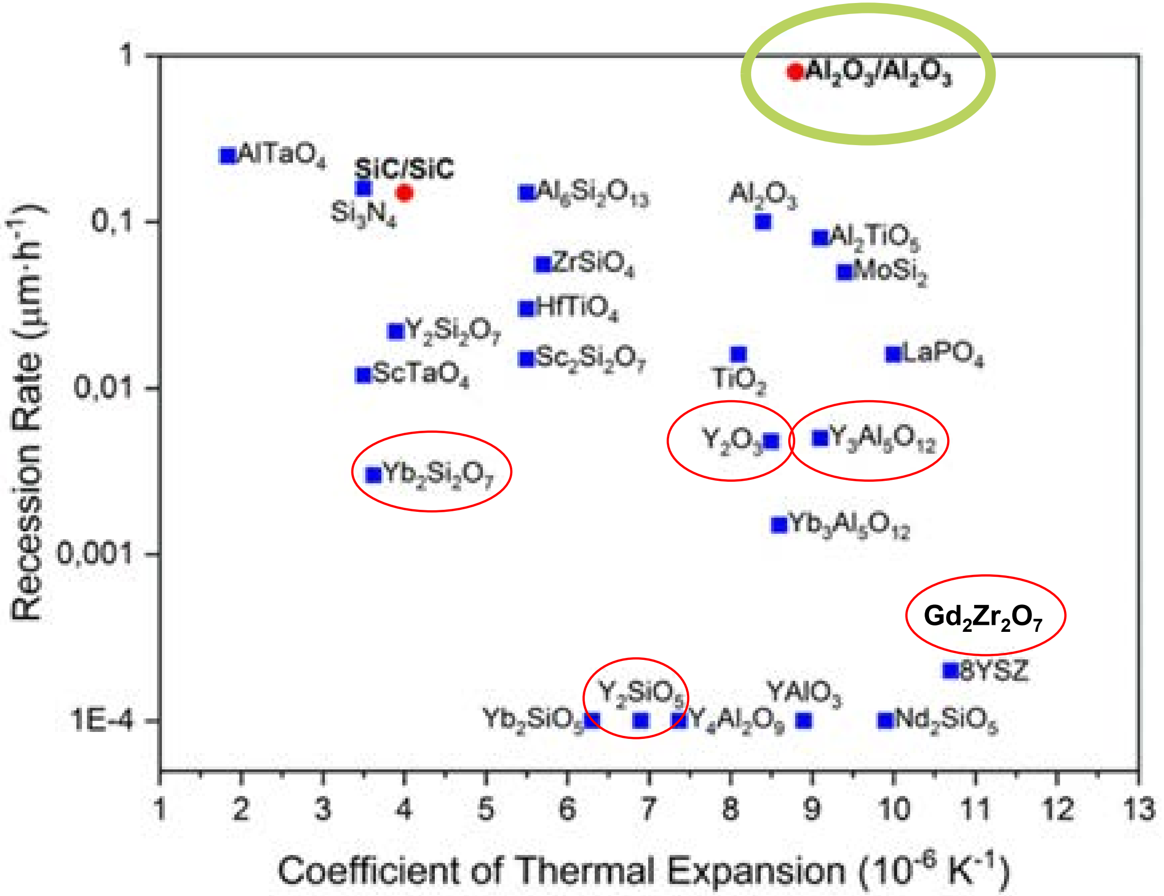
All technologies available in the **Jülich Thermal Spray Center (JTSC)**

EBCS FOR OX-OX CMCS



- Fiber: Nextel 610
- Matrix: 85 % Al_2O_3 + 15 % 3YSZ
- Density: 2,88 g·cm^{-1}
- Porosity: 29 %

W.P. A. Rüdinger, Keramische Zeitschrift, ***03*** *(2013) 166-169*

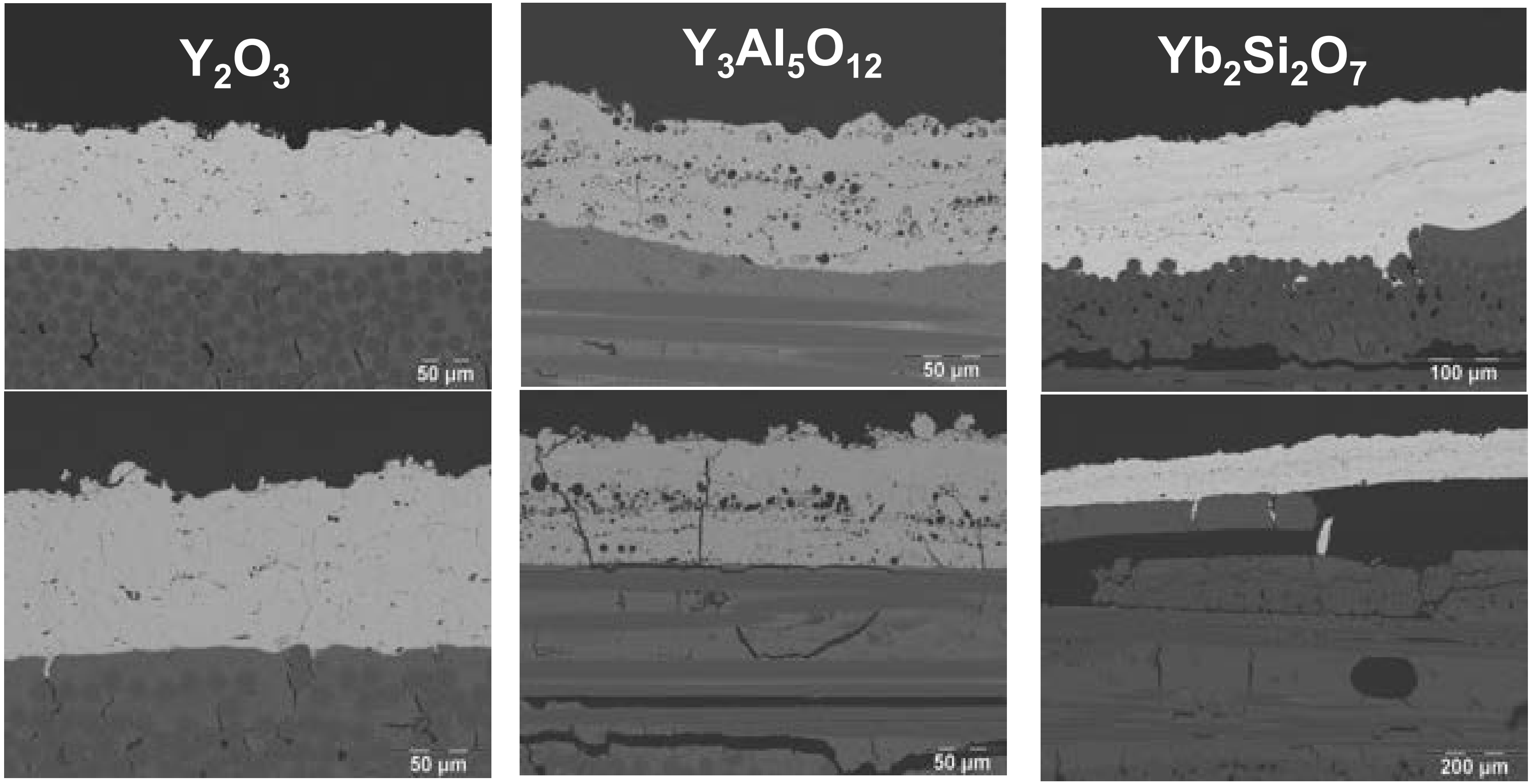


M. Herrmann, H. Klemm, Comprehensive Hard Materials ***2014****, 2, 413-446.*

DIFFERENT EBCS MADE BY APS

As-sprayed

After heat-treatment 4x 20 h, 1200 °C



Good adherence

Cracks at interface large porosity

Delamination due to large TEC mismatch!

R. Vaßen, et al , Coatings 2019, 9, P. 784

EBCS FOR NON OXIDE CMCS

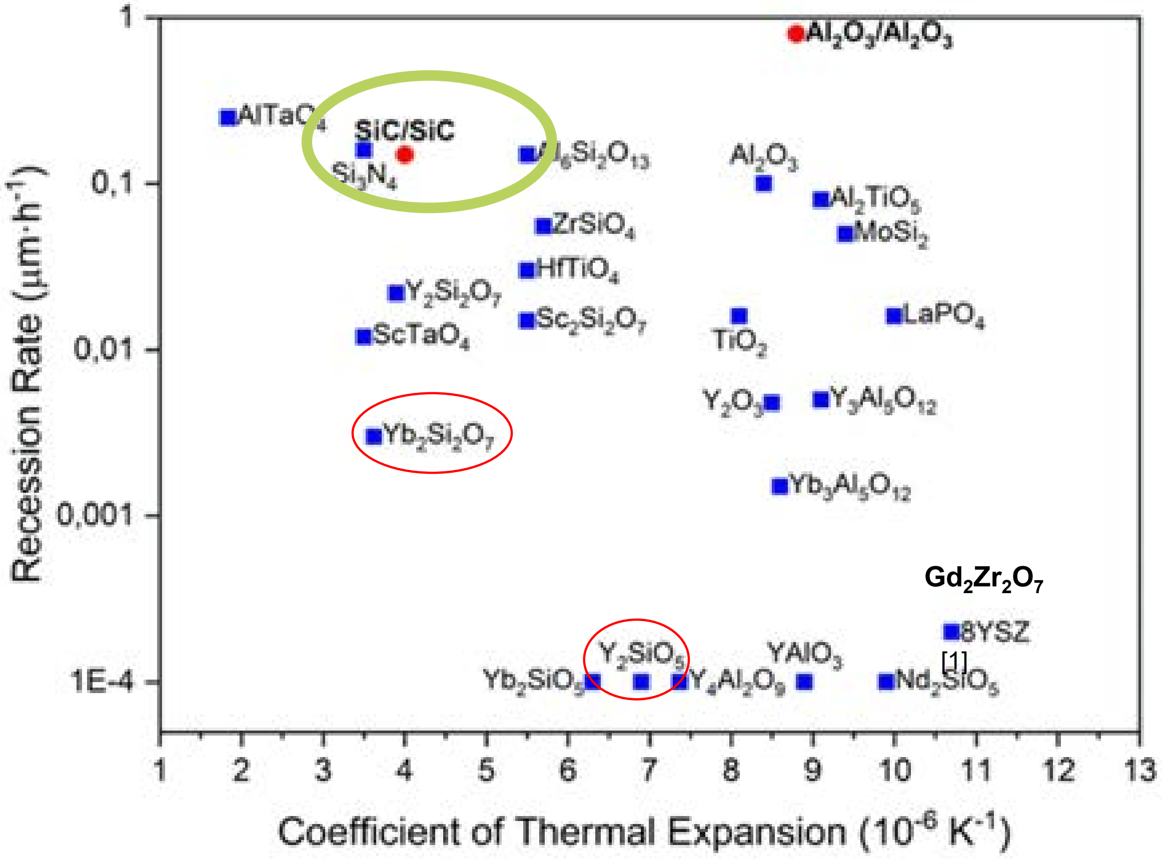
Substrates:

SiC/SiCN CMC, DLR Stuttgart

using Tyranno SA3 SiC fibers

α-SiC HexoloyTM substrates

(Saint Gobain Ceramics, Niagara Falls, NY)



*M. Herrmann, H. Klemm, Comprehensive Hard Materials **2014**, 2, 413-446.*