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Novel Functional Graded Thermal Barrier Coatings in Coal-fired Power Plant Turbines

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- Introduction
- Coating design and fabrication
  - Single ceramic layer (SCL) &Double ceramic layer (DCL) architectures
  - Composite coatings with buffer layers
- Characterization of physical and mechanical properties
  - Microstructure and composition
  - Porosity and hardness
  - Bond strength test
  - Erosion test
- Characterization of thermal property and thermal durability
  - Thermal conductivity, specific heat, coeff. of thermal expansion
  - Thermal shock (TS) test
  - Jet engine thermal shock (JETS) test
  - Furnace cycling thermal fatigue (FCTF) test
  - Thermal gradient mechanical fatigue (TGMF) test
- MD&FE modeling of thermal conductivity; DFT calculation of gas adsorption
- Summary and future work

Limitation of yttria stabilized zirconia

Zirconia partially stabilized with 7~8 wt% yttria (YSZ) is the current state-of-the-art thermal barrier coating material.

The thermal conductivity of 8YSZ is ~2.12 W/m-K @ 800^{o}C. **Lower thermal conductivity materials are required** for future gas turbines.

Above 1200 ^{o}C, YSZ **transforms** from t' phase to the tetragonal and cubic phase (*t* and *c* phases, respectively) during cooling process, and then to monoclinic (*m*) phase with a volume expansion of about 3–5 vol.%, resulting in the spallation or delamination of TBCs.

Additionally, at temperatures above1200 ^{o}C, YSZ layers are prone to **sintering**, which increases thermal conductivity and makes them less effective. The sintered and densified coatings can also **reduce thermal stress and strain tolerance**, which can reduce the coating's durability significantly.

Motivation and objective

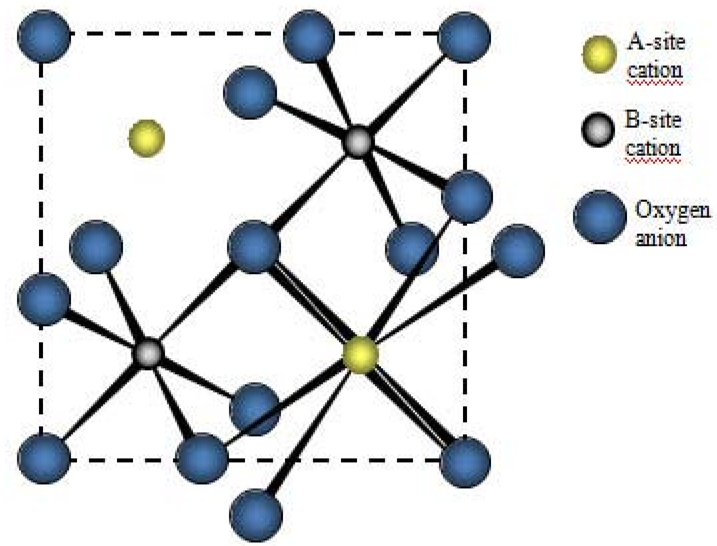
- To further increase the operating temperatures of turbine engines, alternative TBC materials with lower thermal conductivity, higher thermal stability and better sintering resistance are required.

- The objective of the project is to develop a novel lanthanum zirconate ($La_2Zr_2O_7$) based multi-layer thermal barrier coating system.

- The ultimate goal is to develop a manufacturing process to produce pyrochlore oxide based coatings with improved high-temperature properties.

Pyrochlore - $A_2B_2O_7$

Pyrochlore-type rare earth zirconium oxides ($Re_2Zr_2O_7$,Re = rare earth) are promising candidates for thermal barrier coatings, high-permittivity dielectrics, potential solid electrolytes in high-temperature fuel cells, and immobilization hosts of actinides in nuclear waste.

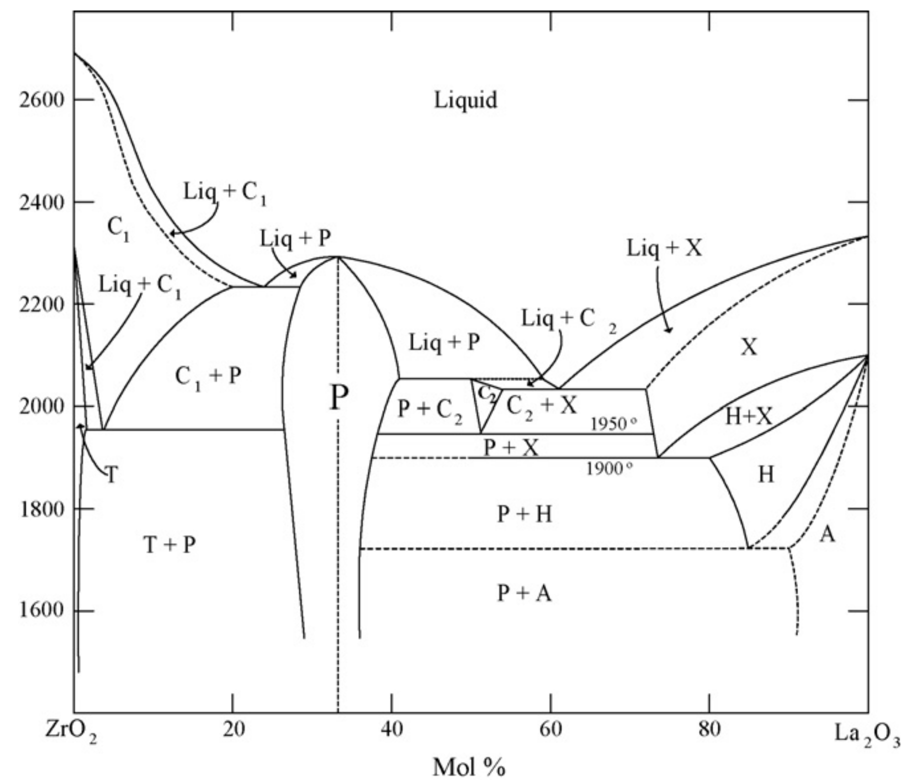


Pyrochlore crystal structure: $A_2B_2O_7$. A and B are metals incorporated into the structure in various combinations. (credit: NETL)

Why $La_2Zr_2O_7$?

Compared with YSZ, $La_2Zr_2O_7$ has

- Lower thermal conductivity
- Higher temperature phase stability. No phase transformation
- Lower sintering rate at elevated temperatures
- Lower CTE



Phase diagram of La_2O_3–ZrO_2

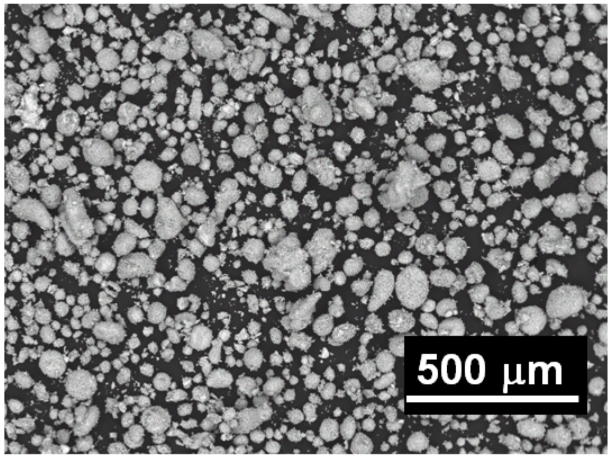
$La_2Zr_2O_7$ vs. YSZ

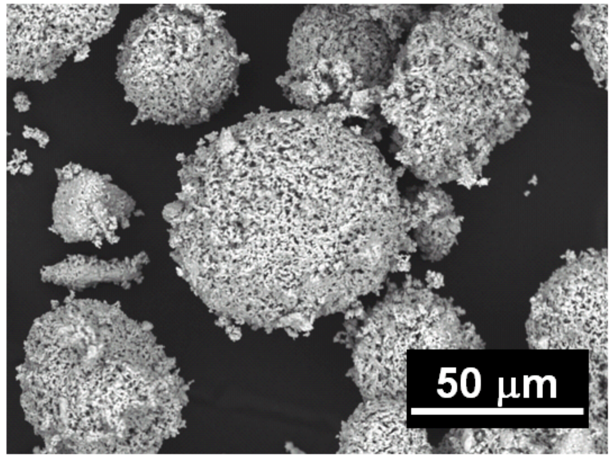
Materials property	8YSZ	$La_2Zr_2O_7$
Melting Point (^oC)	2680	2300
Maximum Operating Temperature (^oC)	1200	>1300
Thermal Conductivity (W/m-K) (@ 800^oC)	2.12	1.6
Coefficient of Thermal Expansion ($x10^{-6}/^oC$) (@1000 ^oC)	11.0	8.9-9.1
Density (g/cm^3)	6.07	6.00
Specific heat (J/g-^oC) (@1000 ^oC)	0.64	0.54

Layered coating architecture

- The coefficient of thermal expansion of $La_2Zr_2O_7$ (~$9x10^{-6}$ /^oC) is lower than those of both substrate and bondcoat (~$15x10^{-6}$/^oC @ 1000 ^oC). As a result, the thermal cycling properties may be a concern
- The layered topcoat architecture is believed to be a feasible solution to improve thermal strain tolerance
- In this work, we develop multi-layer, compositionally graded, pyrochlore oxide based TBC systems

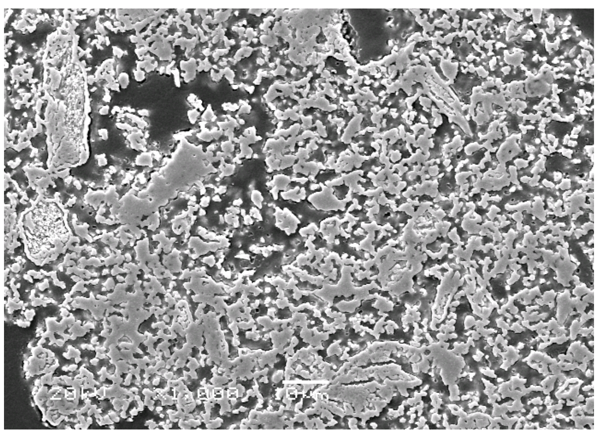
$La_2Zr_2O_7$ spray powder morphology



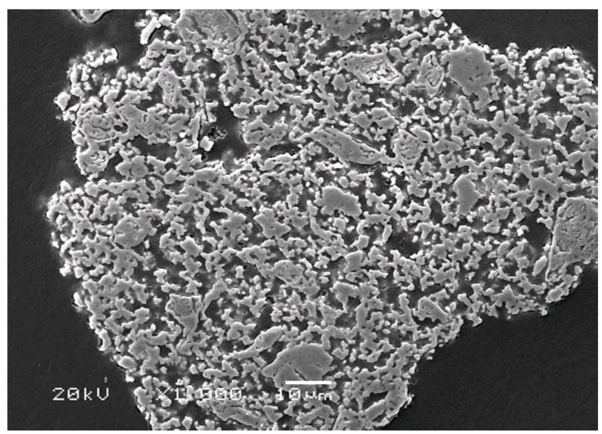


Powder surface morphology

- Spherical shape with a rough surface
- Good flowability and high density
- Particle size between 30 ~ 100 μm



+ 125 um

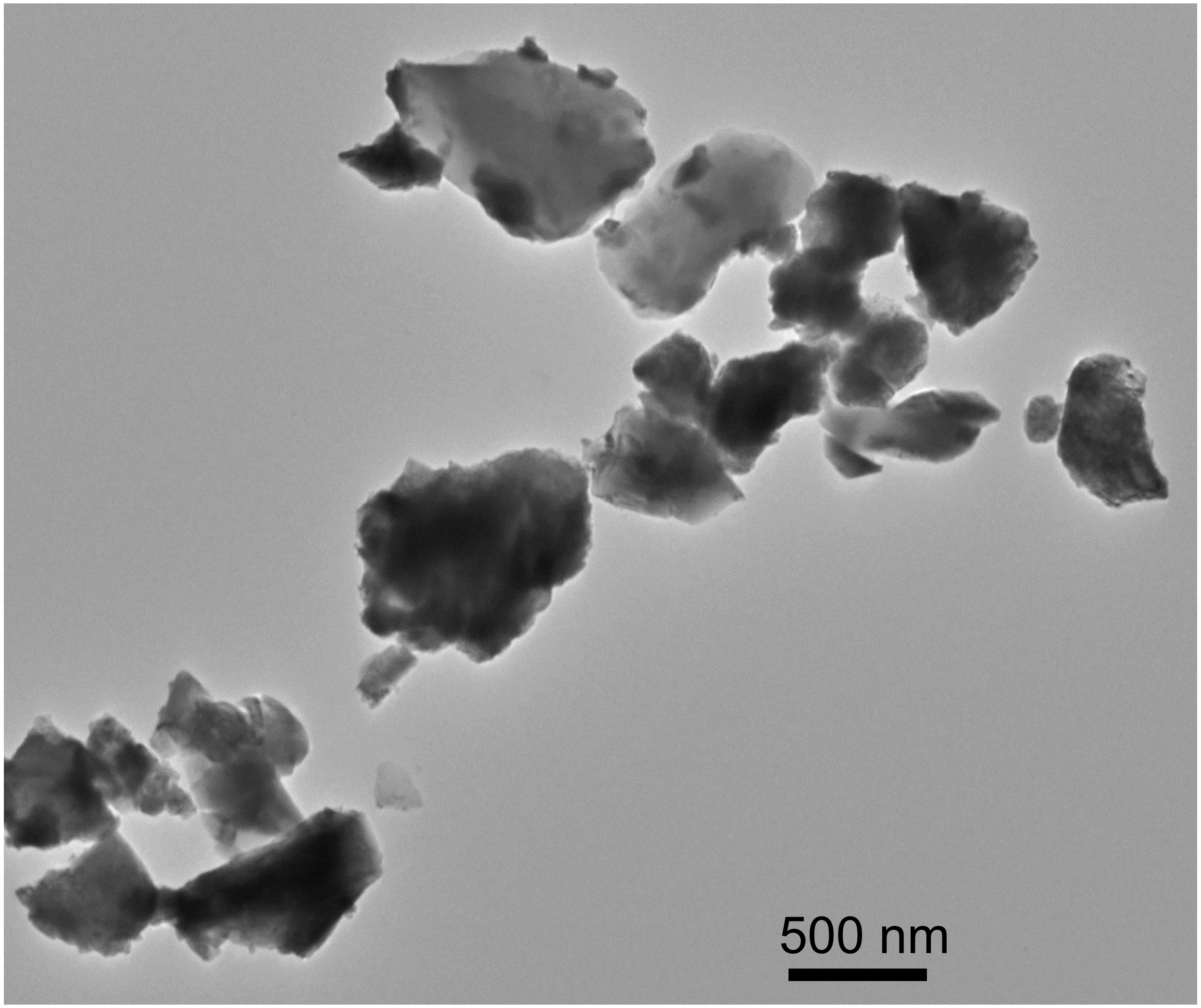


- 125 um

Powder cross-section

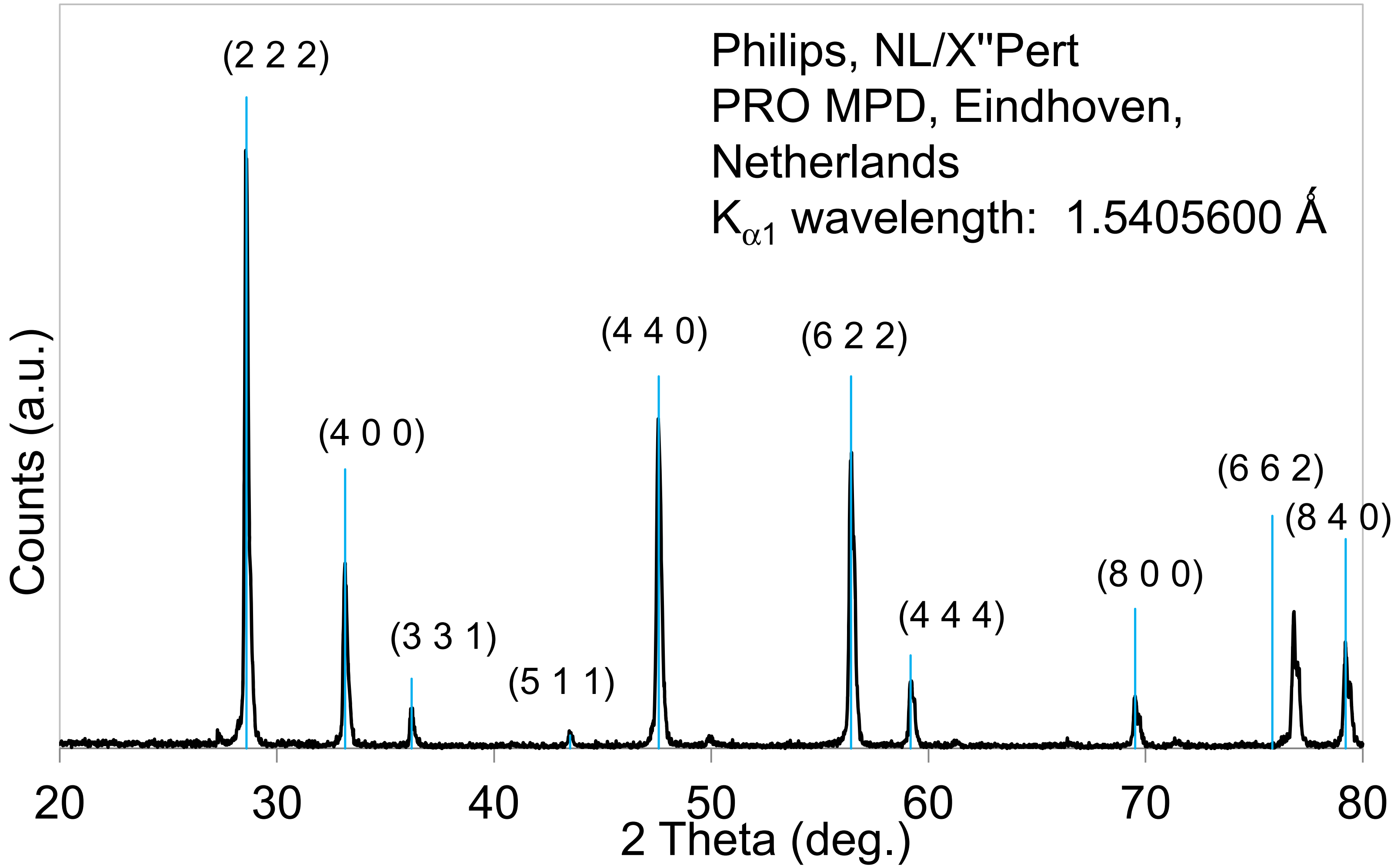
- Porous interior

TEM image of $La_2Zr_2O_7$



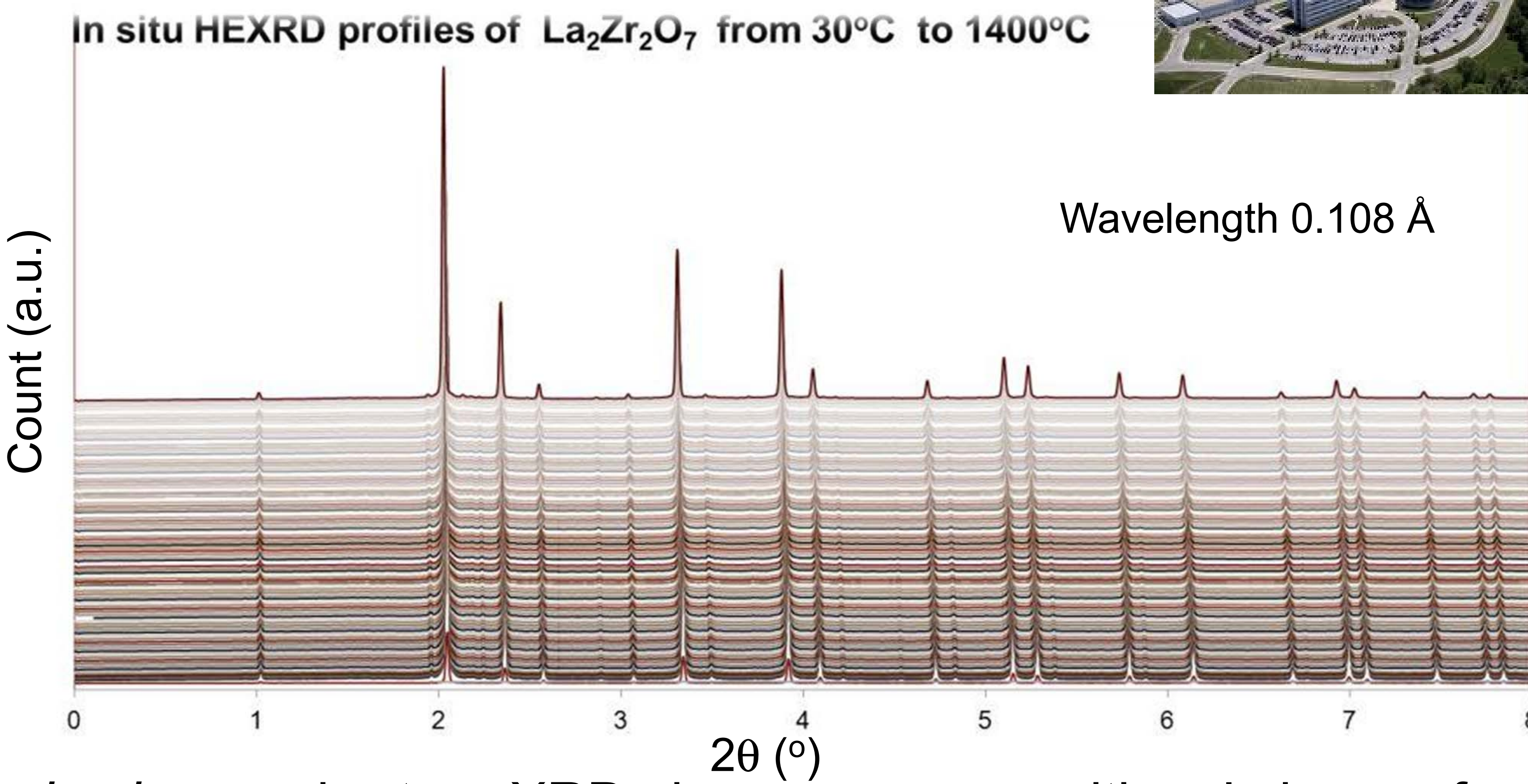
credit: Bin Hu @ Dartmouth

$La_2Zr_2O_7$ powder XRD analysis



XRD data show that the powder composition is $La_2Zr_2O_7$

Synchrotron XRD



in situ synchrotron XRD shows no compositional change from 30 – 1400 °C.

credit: Yang Ren @ ANL

Coating fabrication using APS

- $La_2Zr_2O_7$ coatings were deposited using air plasma spray (APS) technique by a Praxair patented plasma spray torch.
- Haynes 188 superalloy was used as the substrate.

Haynes 188	Co	Ni	Cr	W	Si	C	La	Fe	Mn
(w%)	39	22	22	14	0.35	0.10	0.03	3	1.25

- The bond coat is Ni-based intermetallic LN-65 using APS, with a thickness of 228 μm

LN-65	Ni	Cr	Al	Y	O
(w%)	67.3	21.12	9.94	1.02	0.19

- Controlled spray parameters:
  - Powder feed ratio
  - Torch current
  - Torch gas (Argon), Carrier gas (Argon), Shield gas (Argon), Secondary gas (Hydrogen)
  - Standoff distance
  - Sample rig surface rotation speed (RPM and surface speed)

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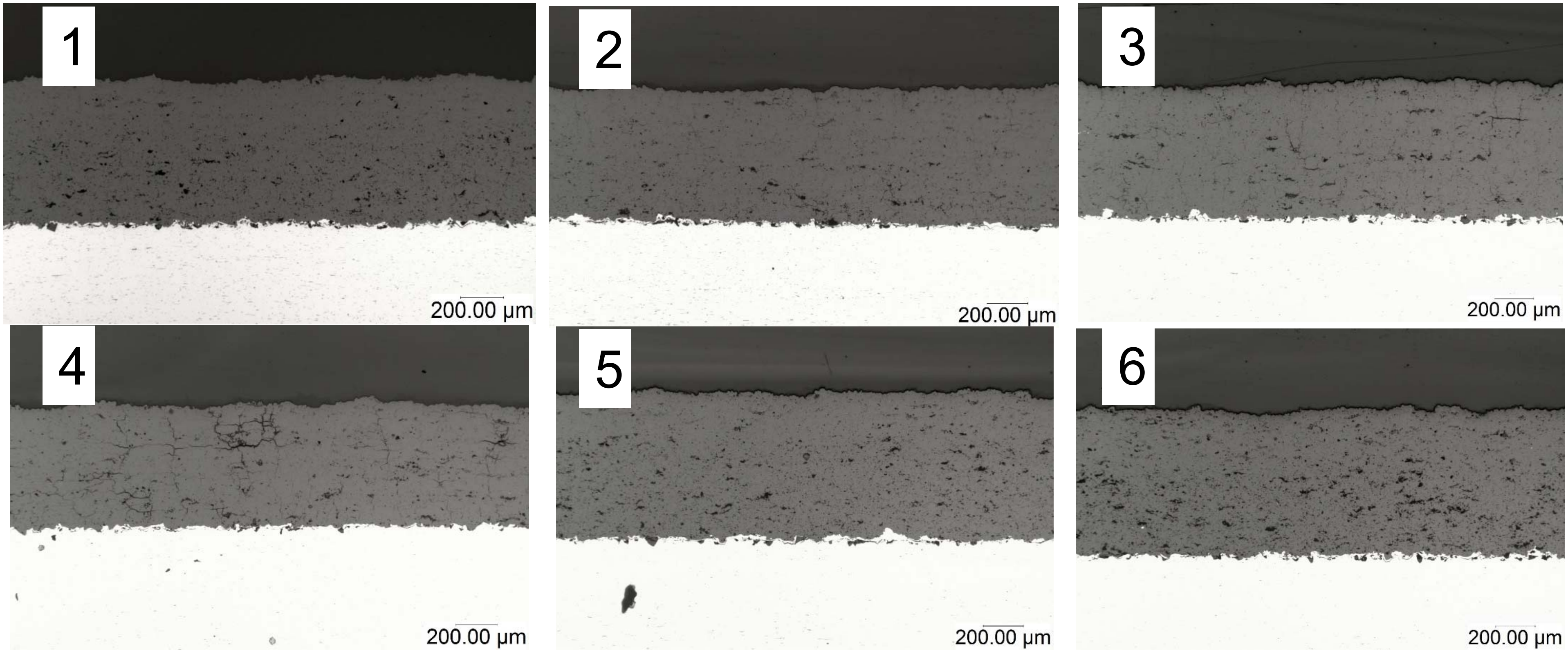
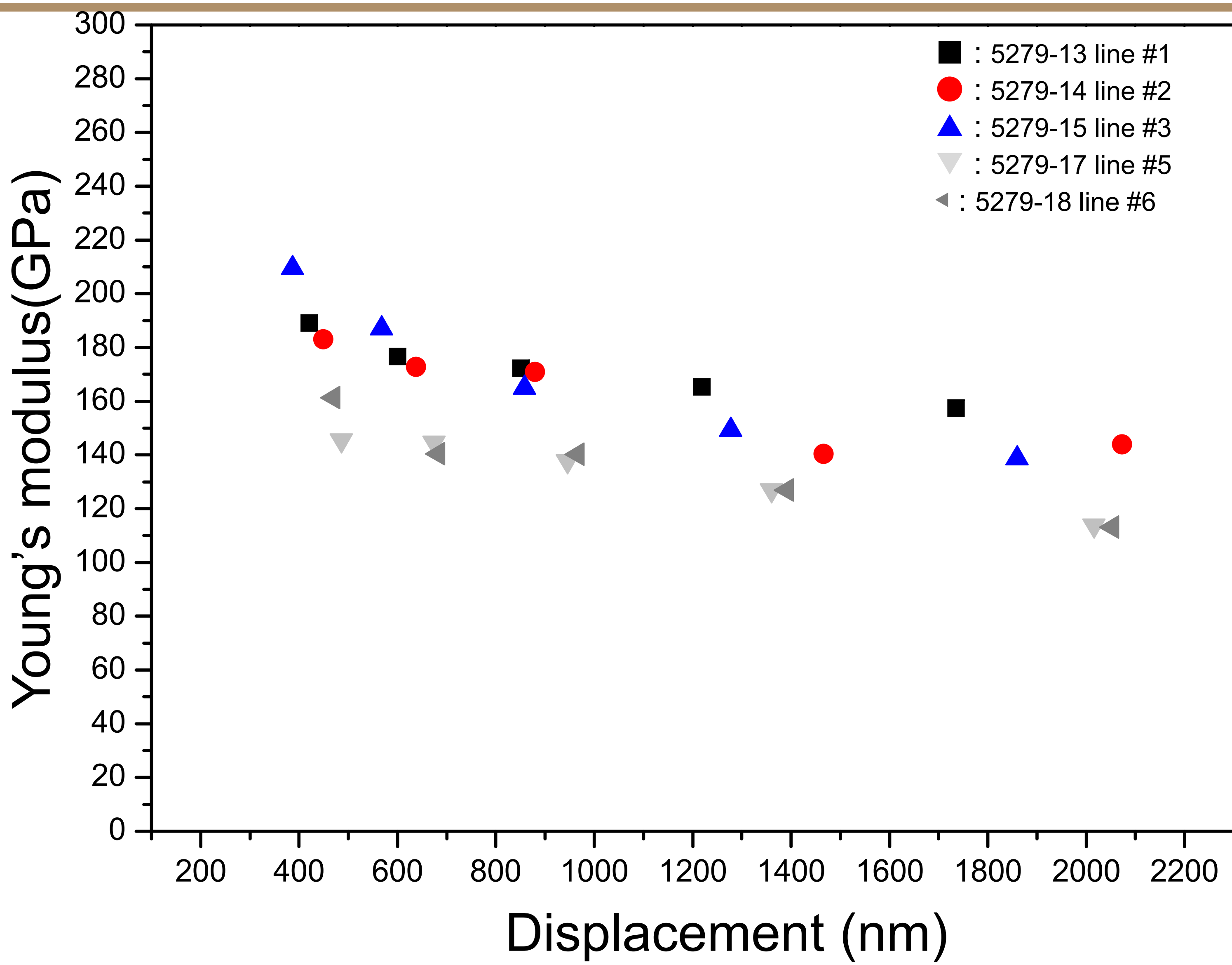
Cross sectional view of dense coating

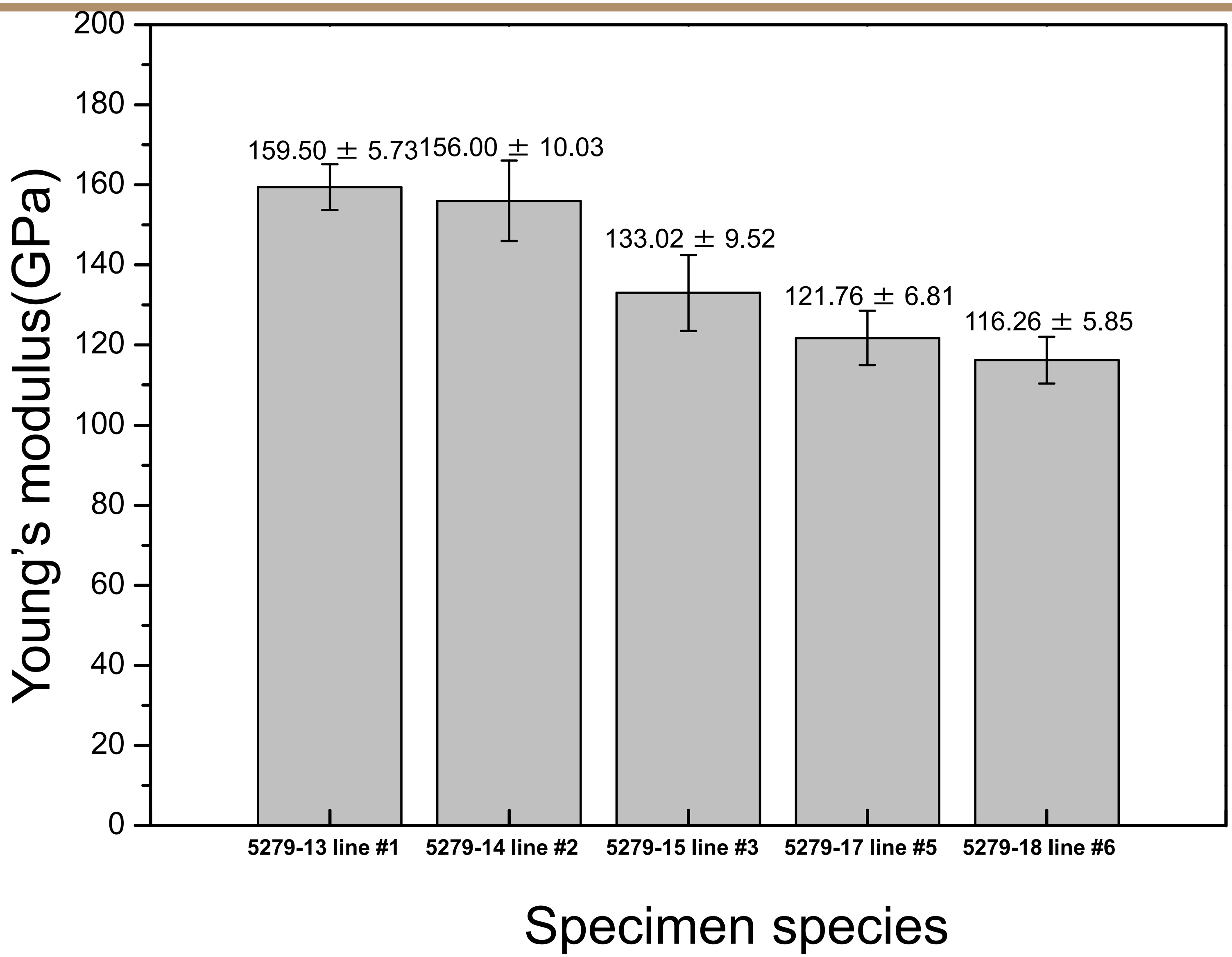


Processing parameters (powder feeding rate, surface speed, current, stand off) were varied to control the porosity.

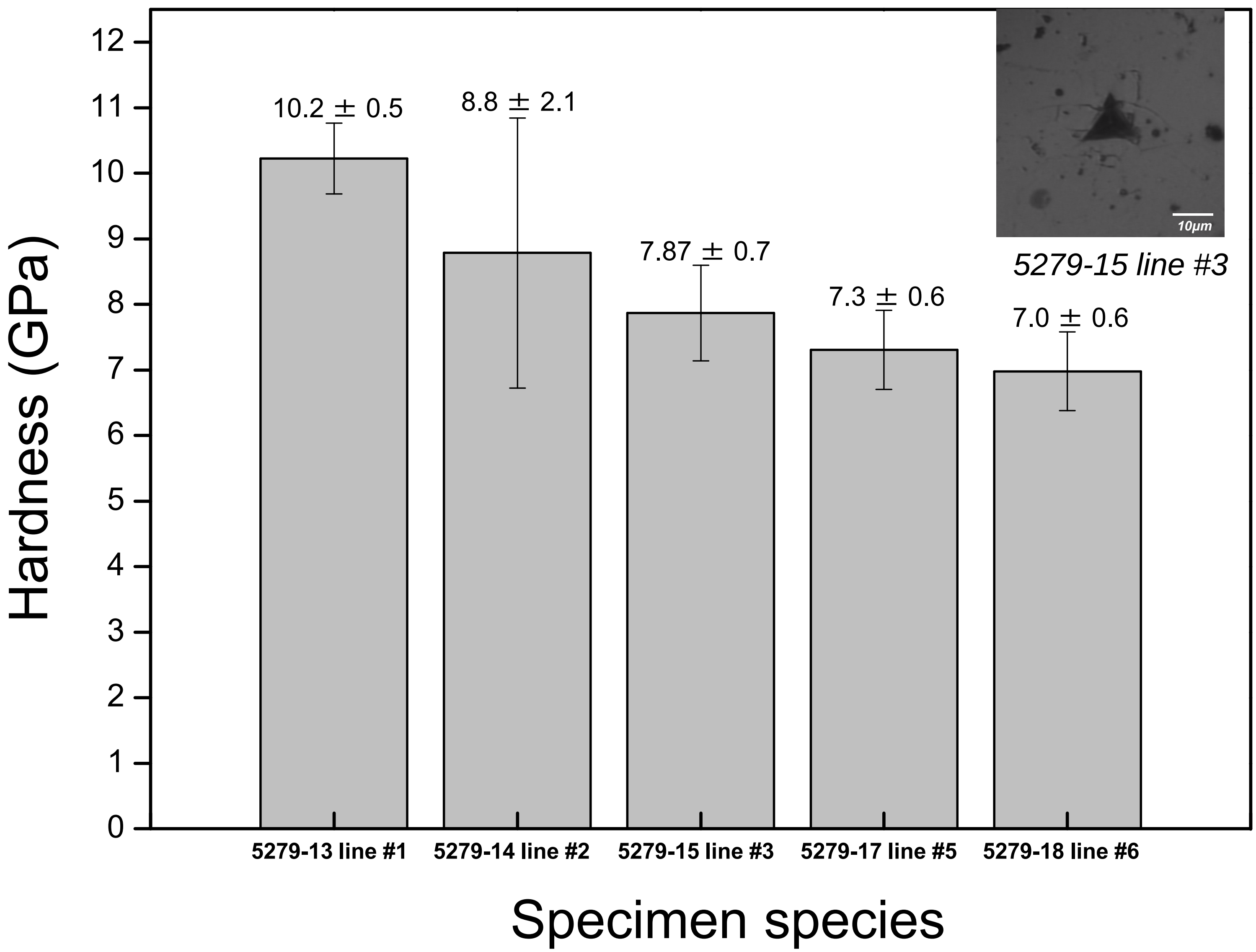
Nanoindentation Young's modulus vs. displacement



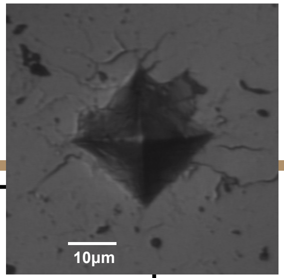
Nanoindentation Young's modulus



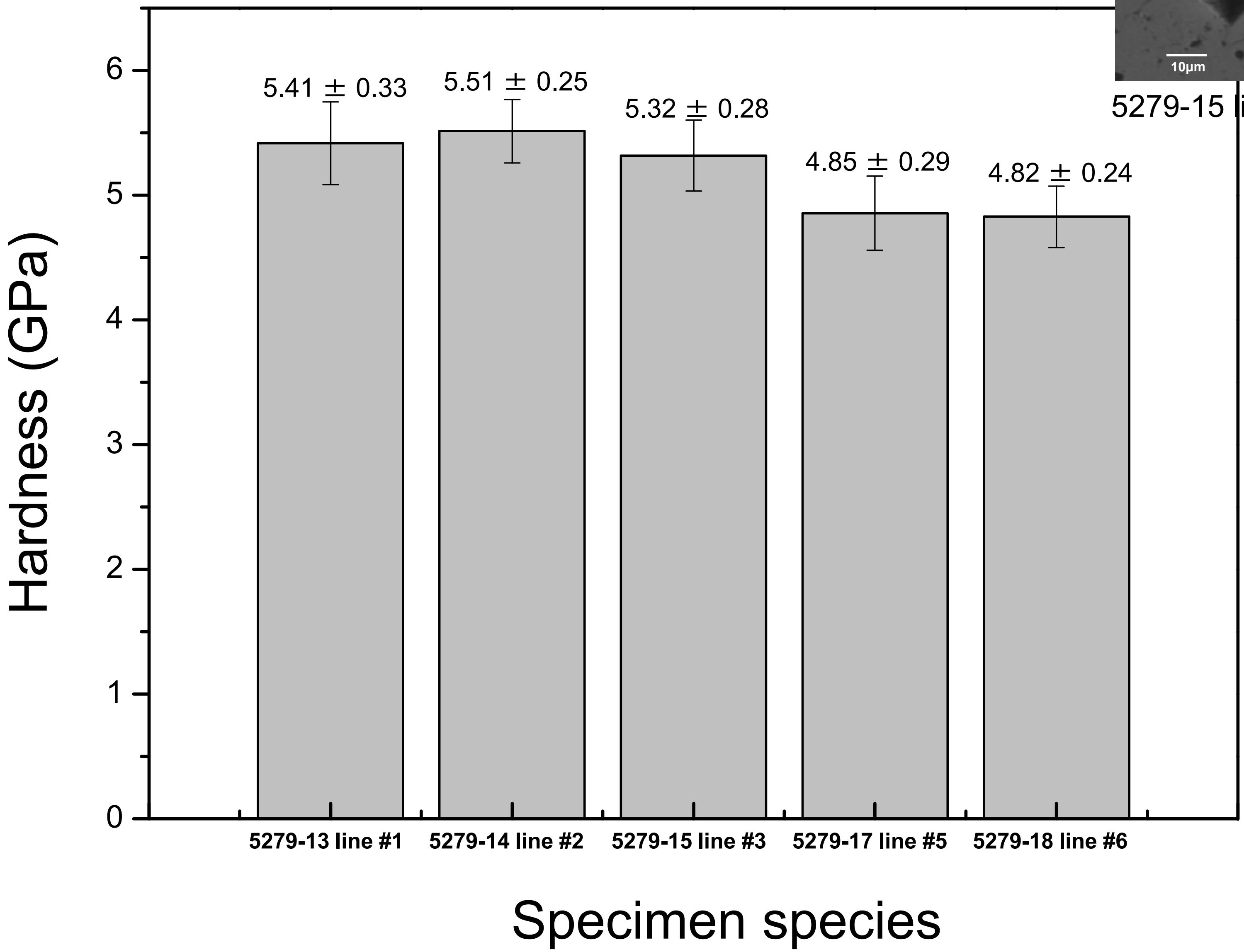
Nanoindentation hardness



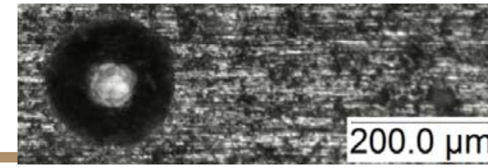
Vicker’s indentation hardness

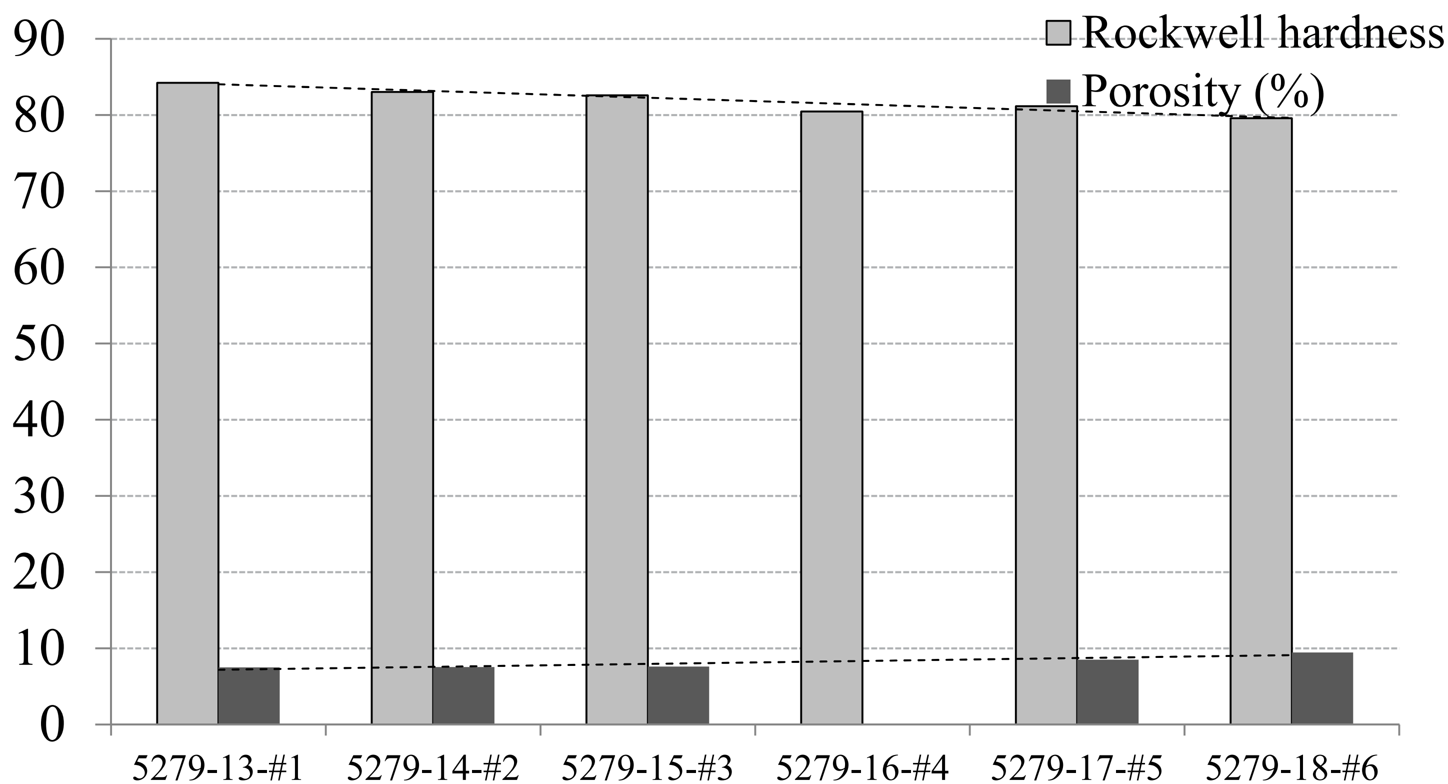


5279-15 line #3



Rockwell's indentation hardness





- Low density coatings with porosity between 7~10 % were achieved.
- Porosity and hardness can be tuned via changing processing conditions
- Powder feed rate↑ or current↓ → porosity↑ → hardness↓
  [Hardness = 1.99 × (100-porosity) -100]

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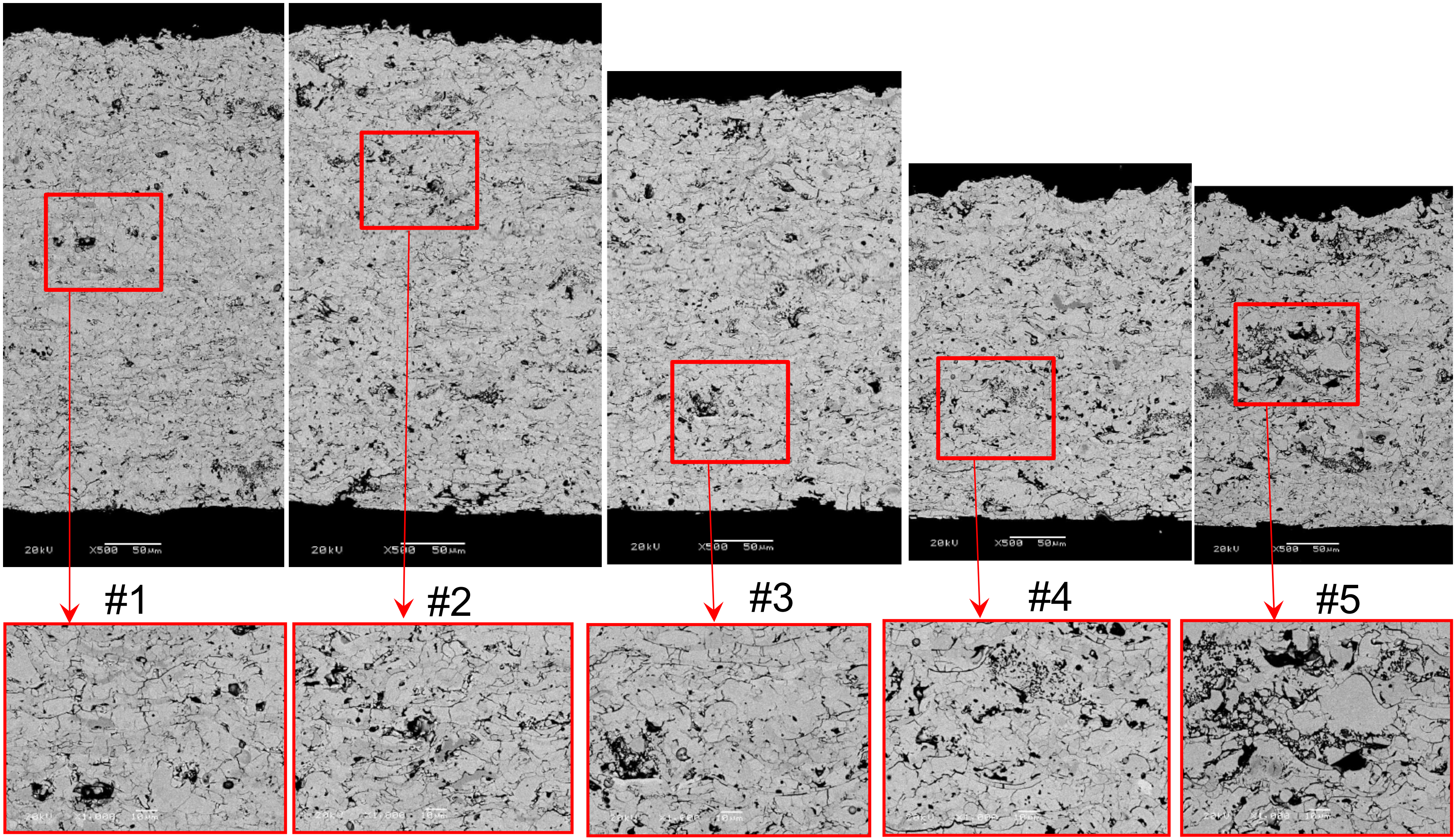
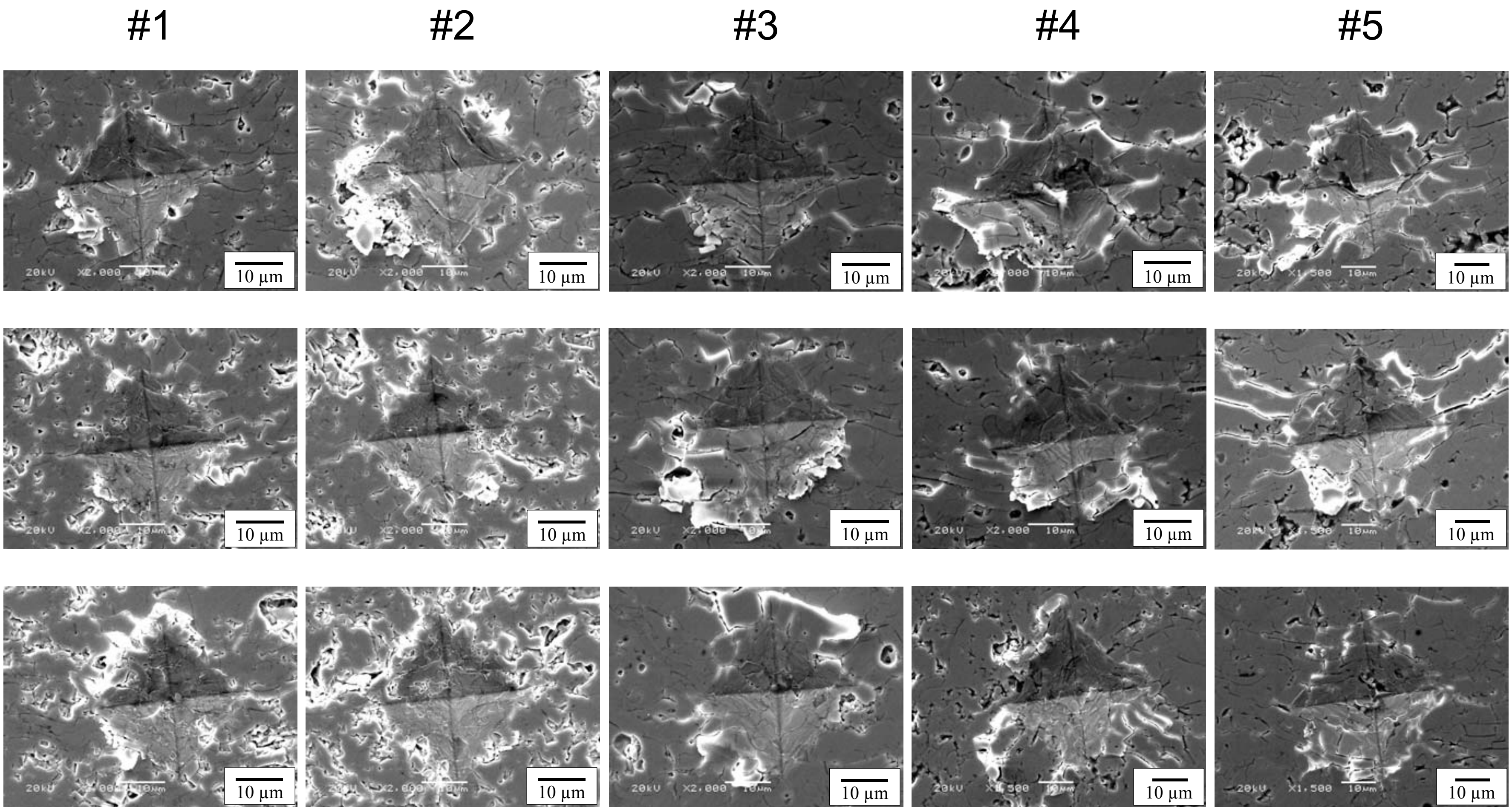
Cross sections of SCL $La_2Zr_2O_7$ coatings

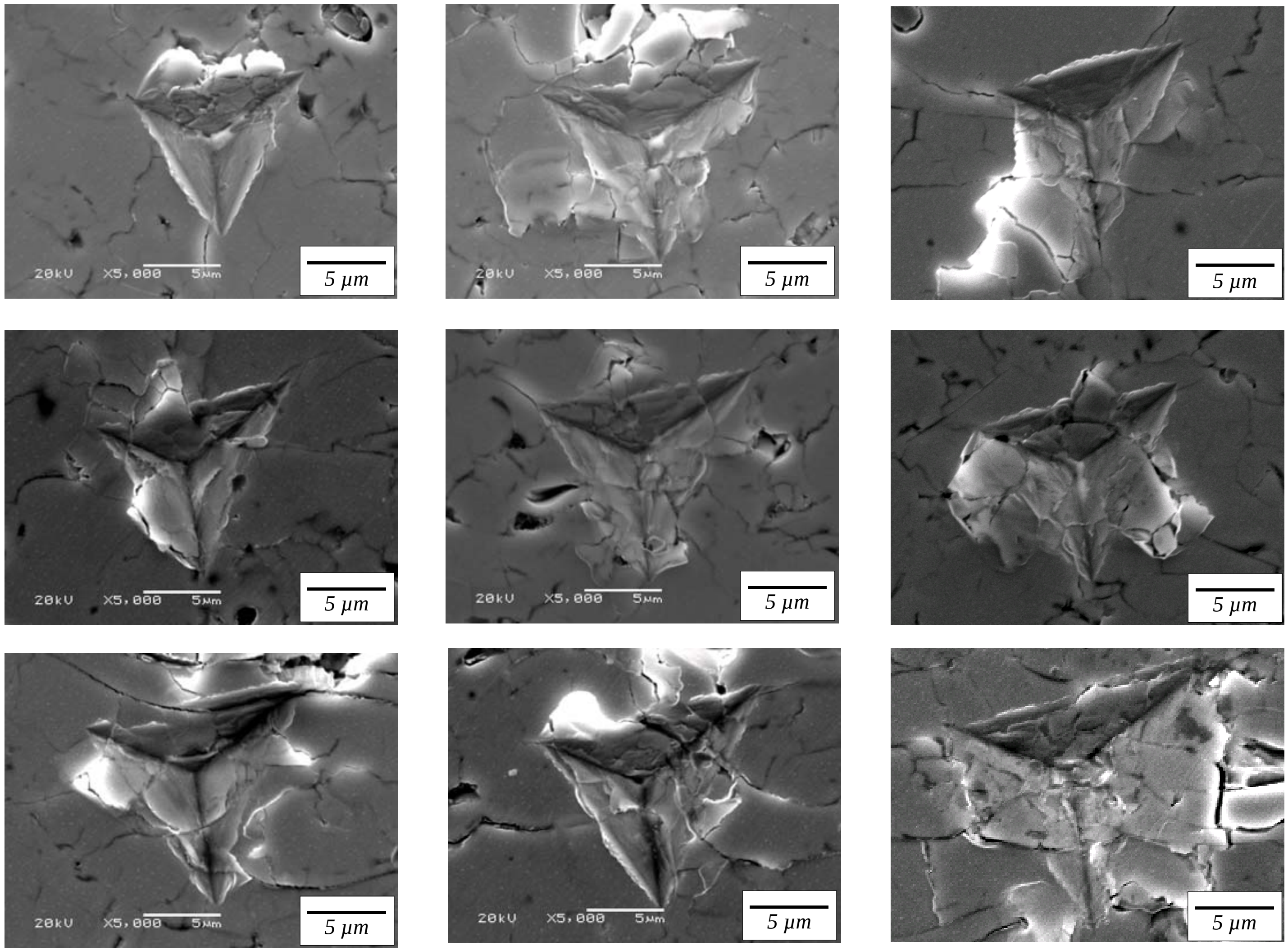


Vickers hardness indentation

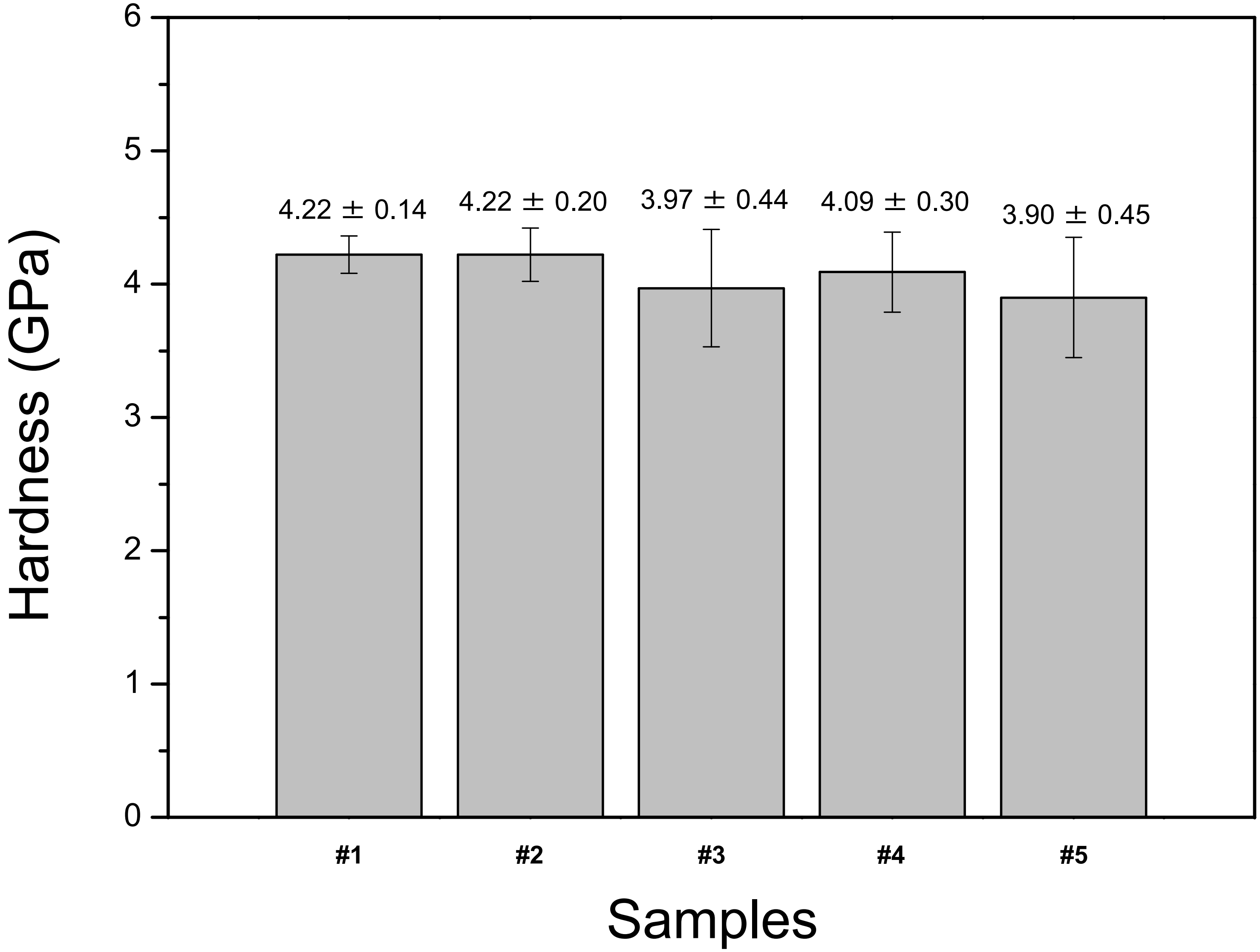


Nanoindentation

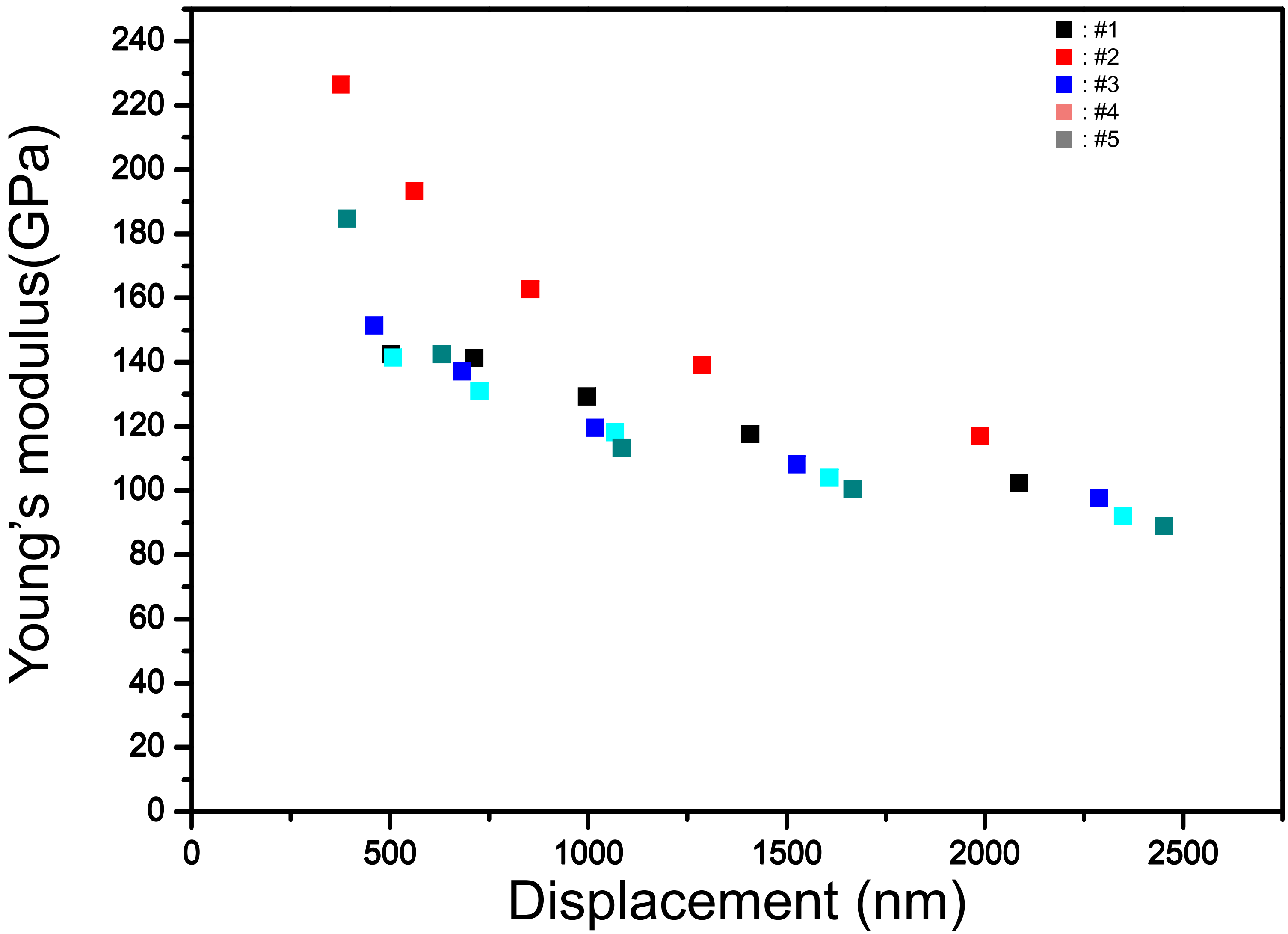
#3 #4 #5



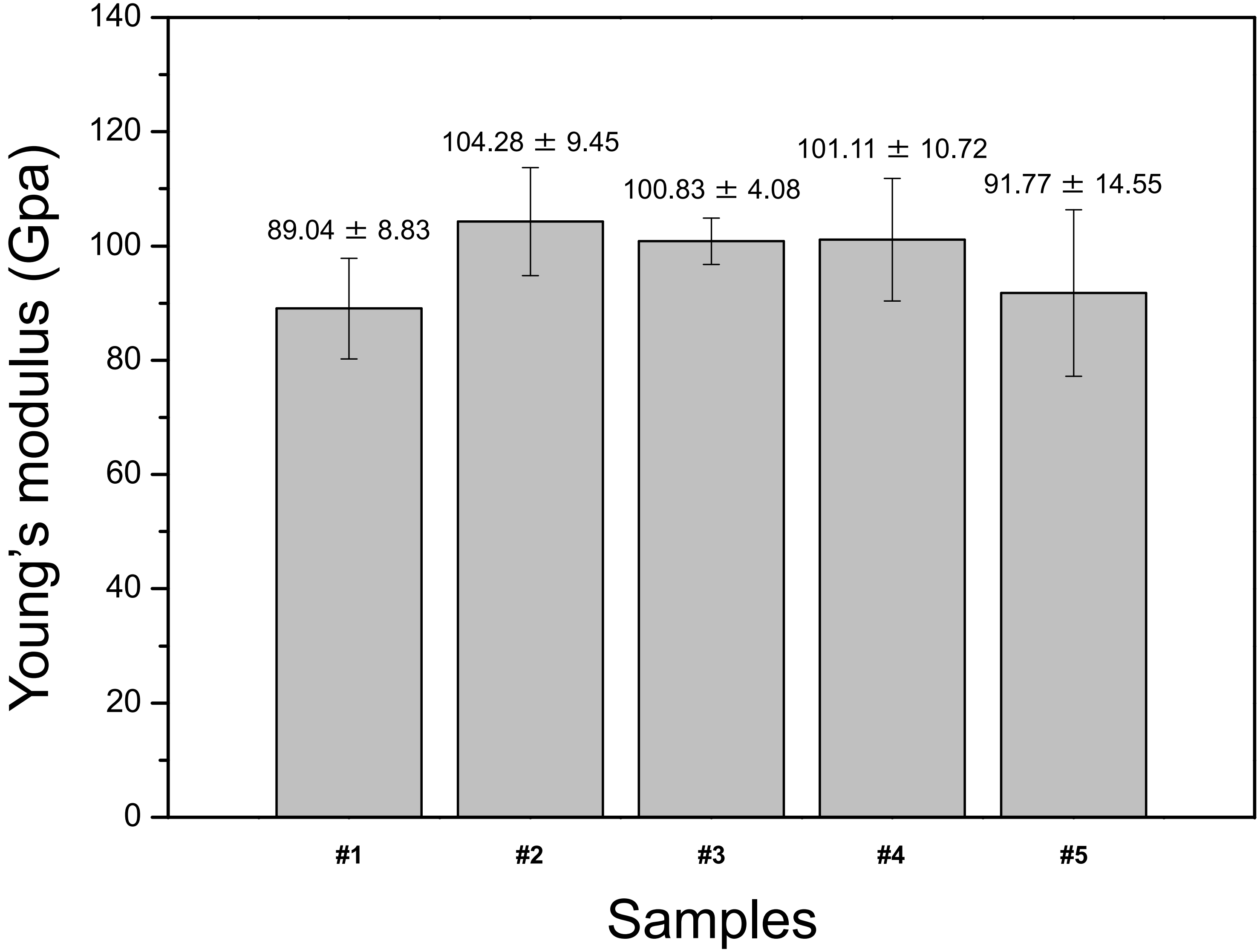
Vickers indentation hardness



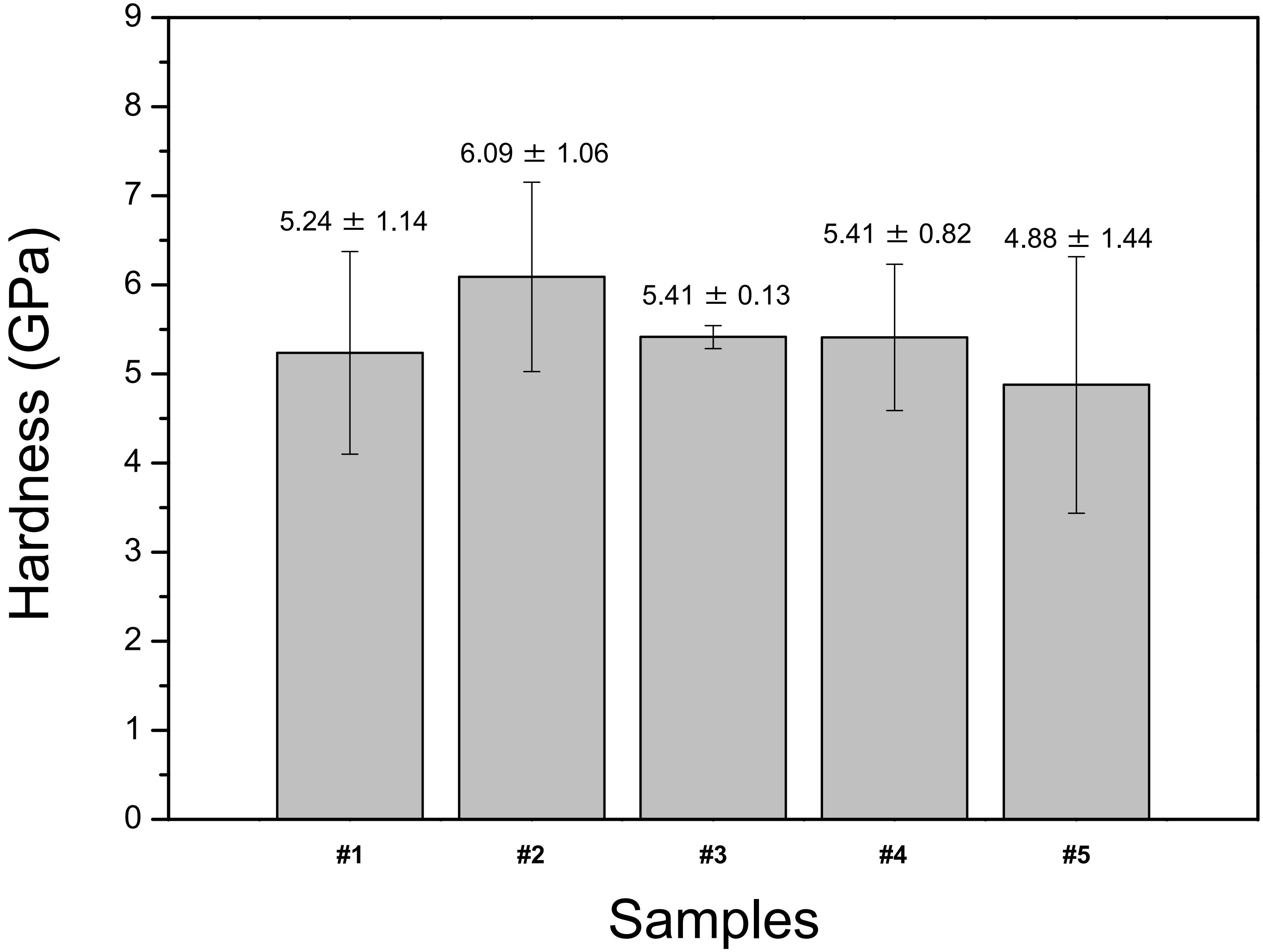
Nano indentation Young's modulus vs. displacement



Nanoindentation Young's modulus



Nanoindentation hardness



Porosity of low density SCL coating

Line #	Density (g/cm^3)	Porosity (%)
7	5.3182	11.36
8	5.2587	12.36
9	5.2584	12.36
10	5.2917	11.81
11	5.2614	12.31
12	5.0089	16.52

Low density coatings with porosity between 11~17% were achieved.

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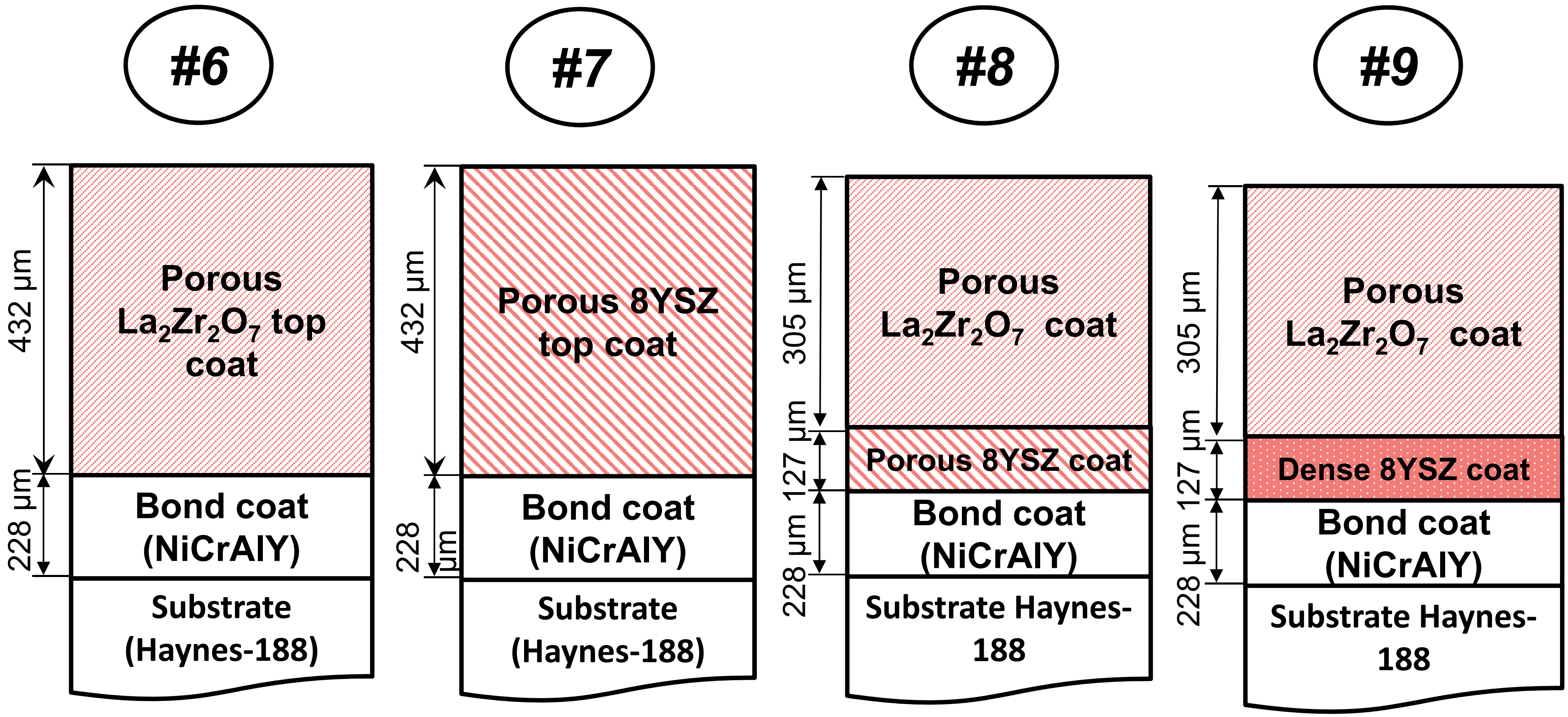
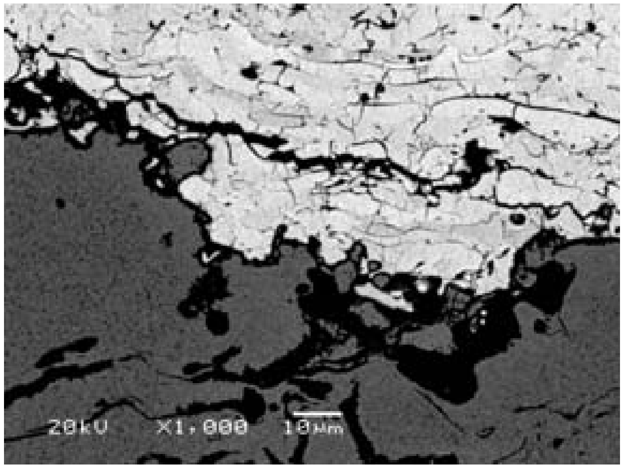
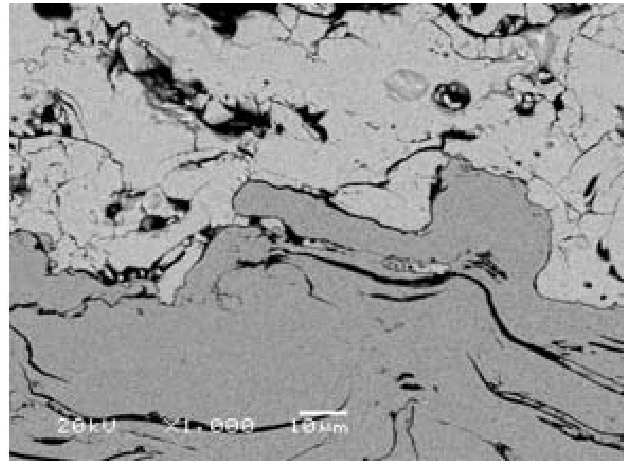
Double ceramic layer (DCL) architectures



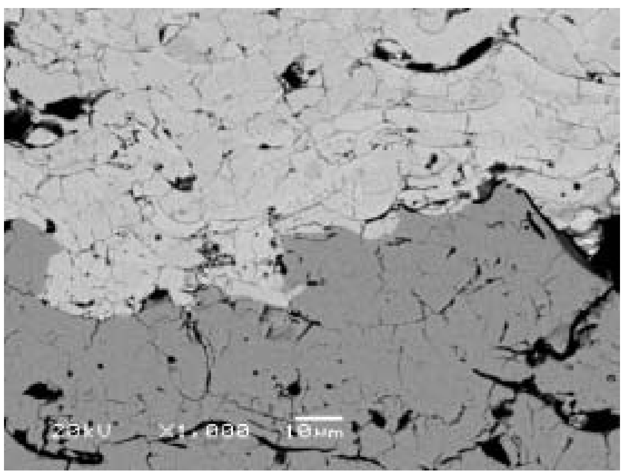
Interfaces of DCL coatings



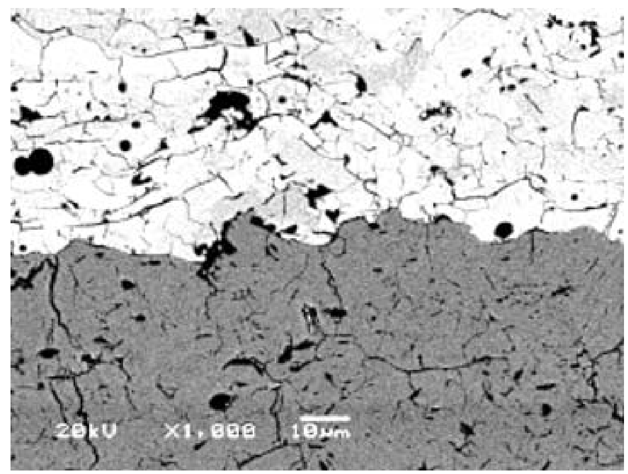
#6 $La_2Zr_2O_7$ and bond coat interface



#7 porous 8YSZ and bond coat interface



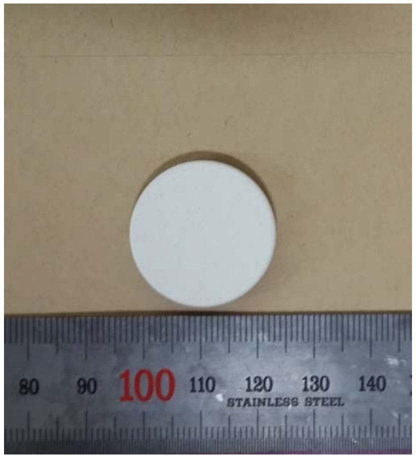
#8 $La_2Zr_2O_7$ and porous 8YSZ interface



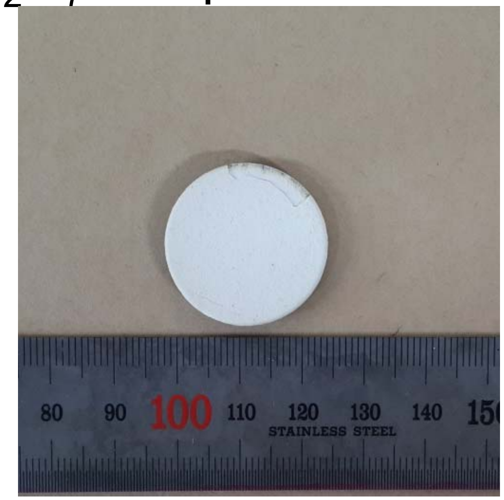
#9 $La_2Zr_2O_7$ and dense 8YSZ interface

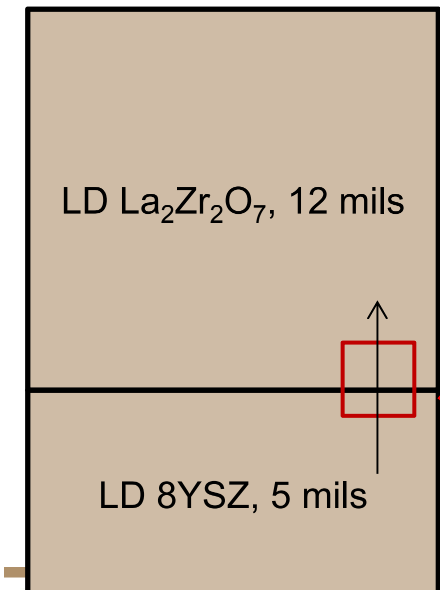
Energy-dispersive X-ray spectroscopy

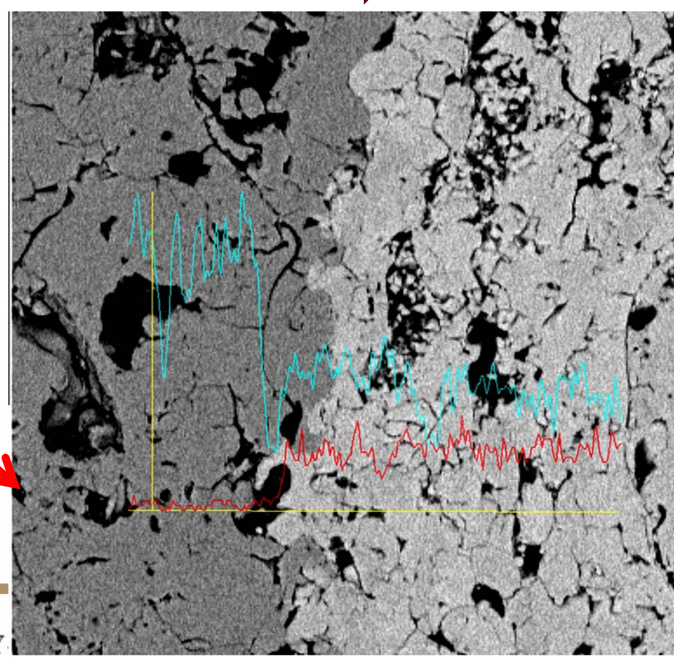
Applied heat treatments on sample #8: 8 $La_2Zr_2O_7$ and porous 8YSZ

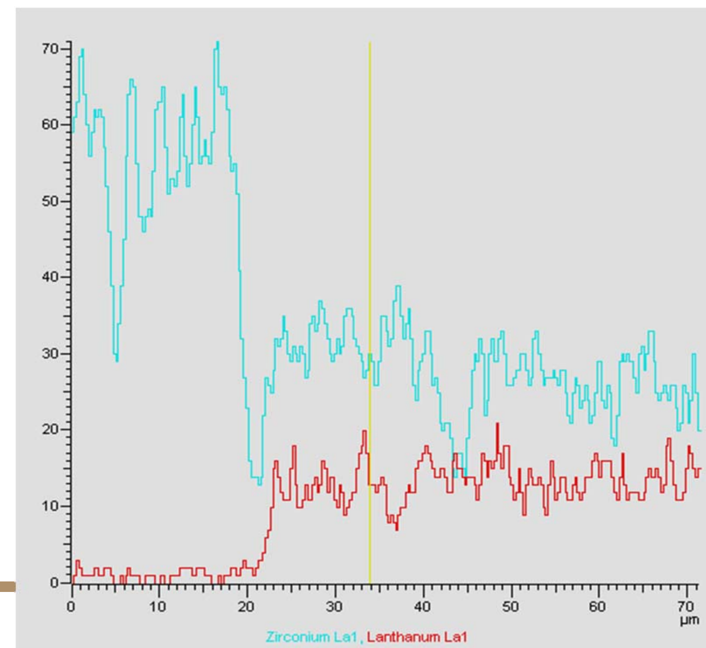


Heat treatment
1080℃ 4h
Ar atmosphere

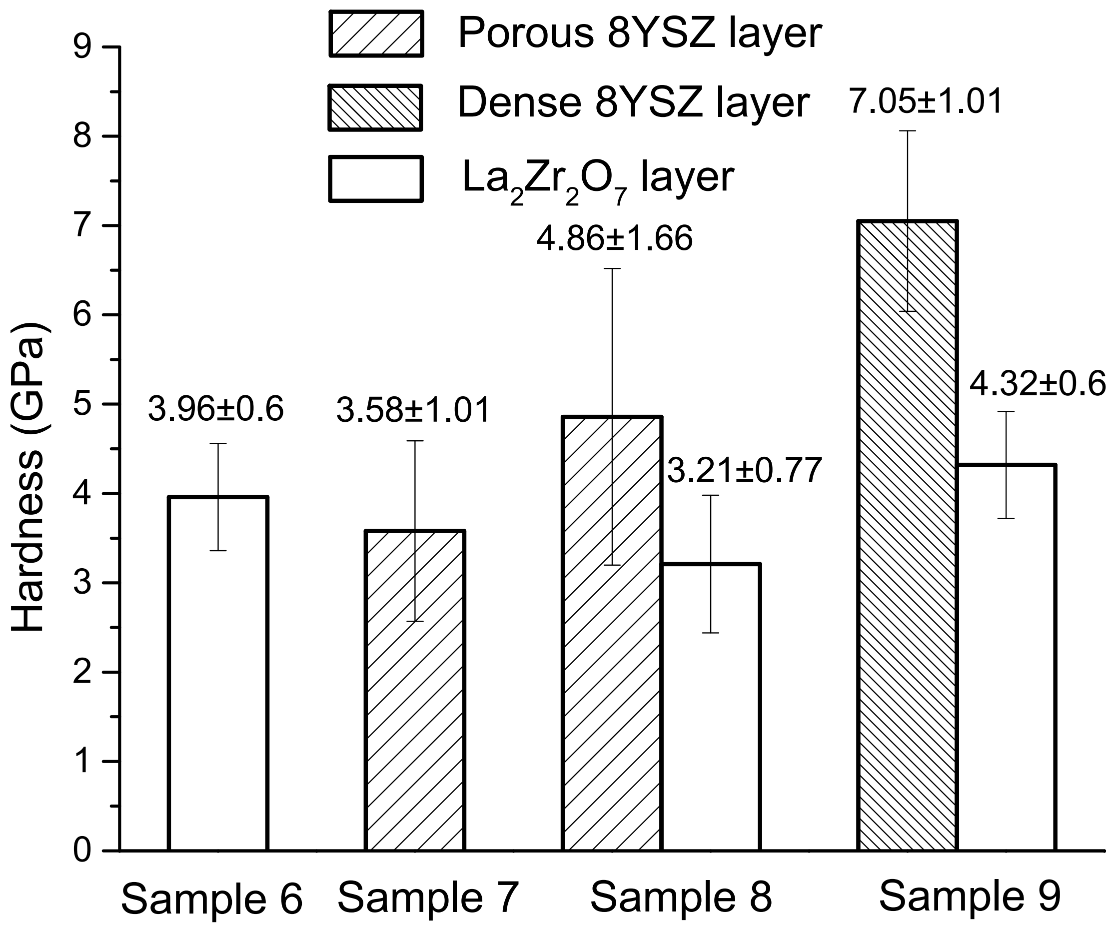








Vickers hardness of DCL coatings



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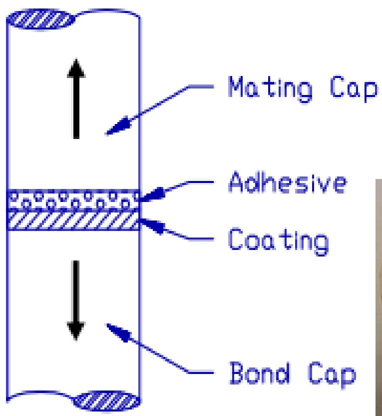
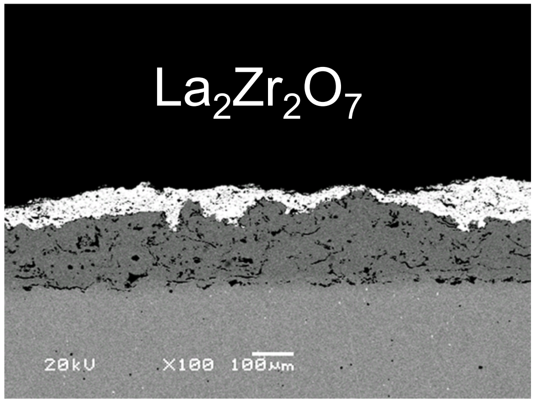
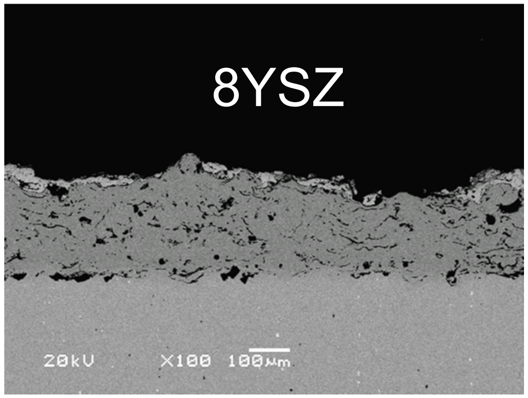
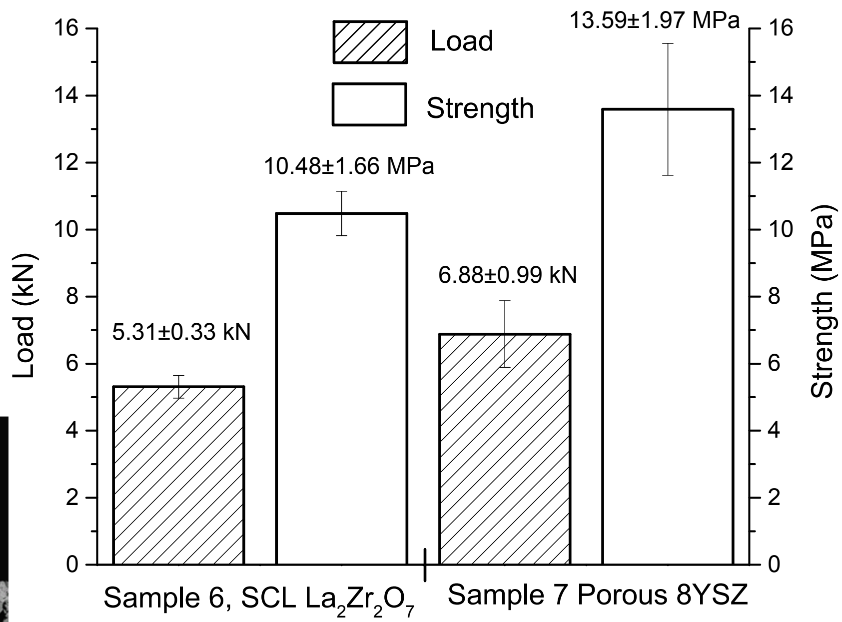
Bond strength test

Epoxy (FM 1000 adhesive film) to glue coating buttons to a mating cap.
Tensile test according to ASTM-C-633.

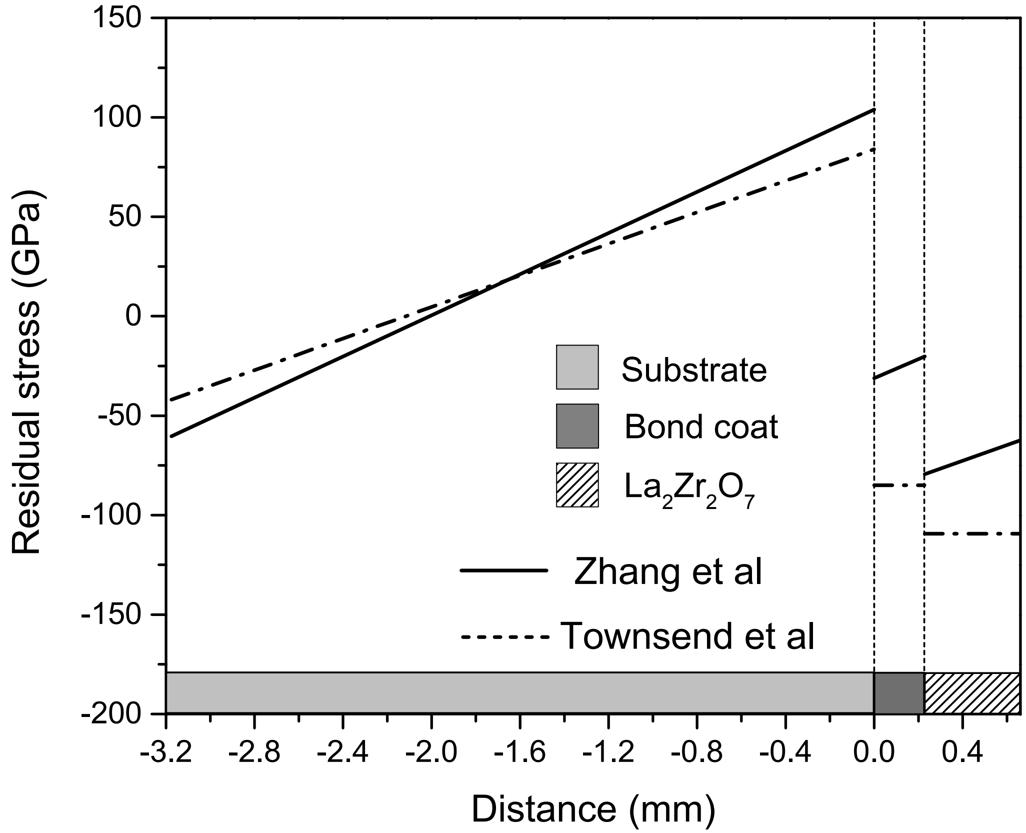








Residual stress distribution in coating



$$\sigma_s = E_s\left[\varepsilon_s + K\left(z+\delta\right)\right]$$

$$\sigma_i = E_i\left[\varepsilon_i + K\left(z+\delta\right)\right]$$

where $\varepsilon_i = \Delta\alpha\Delta T + \sum_{k=1}^{n}\frac{E_k t_k}{E_s t_s}(\alpha_k - \alpha_i)\Delta T$

$$\varepsilon_s = -\sum_{i=1}^{n}\frac{E_i t_i}{E_s t_s}\Delta\alpha\Delta T$$

$$\delta = \frac{t_s}{2} - \sum_{i=1}^{n}\frac{E_i t_i}{E_s t_s}\left(2h_{i-1} + t_i\right)$$

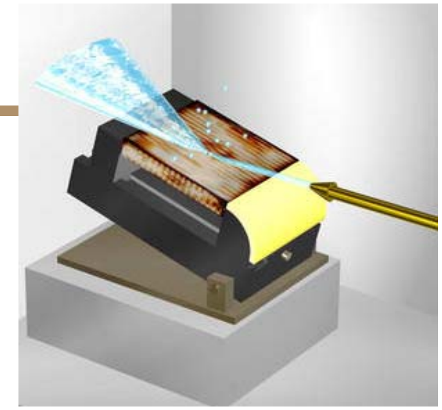
$$K = -\sum_{i=1}^{n}\frac{6E_i t_i \Delta\alpha\Delta T}{E_s t_s^{\,2}}$$

where α is the coefficient of thermal expansion (CTE), k is the ceramic coating layers range from 1 to n, t_i is the thickness of i^{th} layer.

X.C. Zhang, Thin Solid Films, 488 (2005) 274-282.

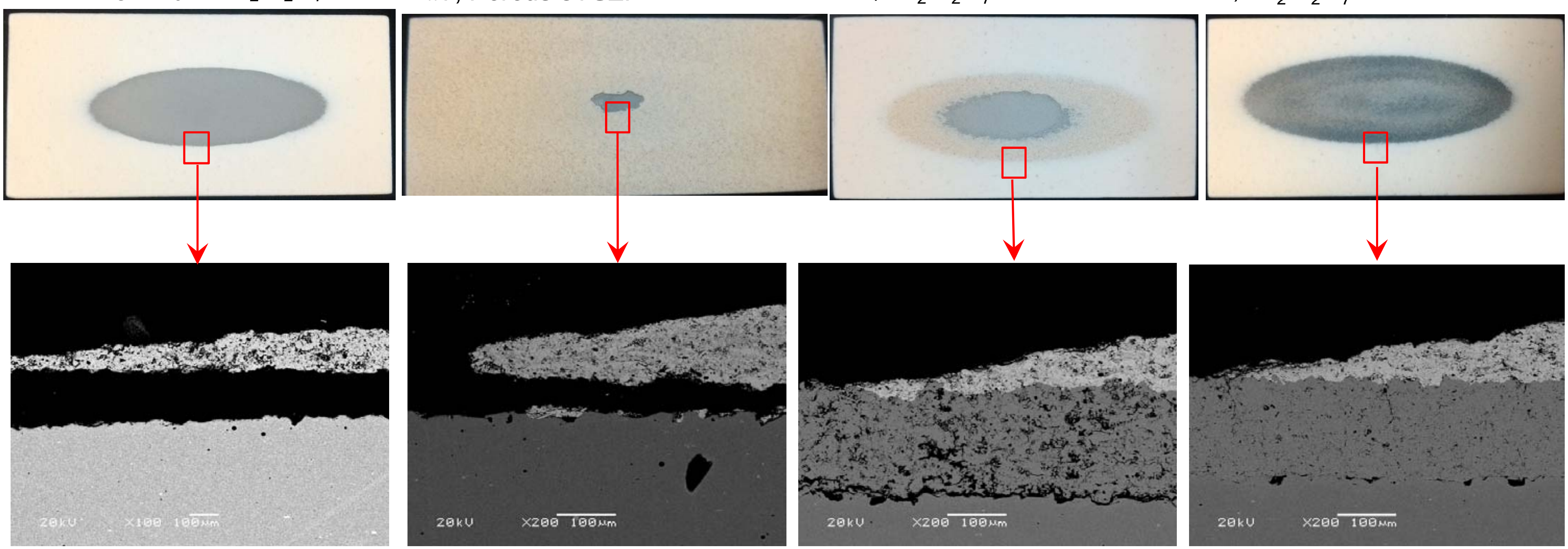
Guo *et al.,* Thermal properties, thermal shock and thermal cycling behavior of lanthanum zirconate based thermal barrier coatings, *Metallurgical and Materials Transactions E*, (DOI: 10.1007/s40553-016-0070-4)

Erosion test



- 600±0.2g alumina sands with a diameter of 50 μm
- Spray rate 6 g/s; duration 100 s; spray angle 20^{o}

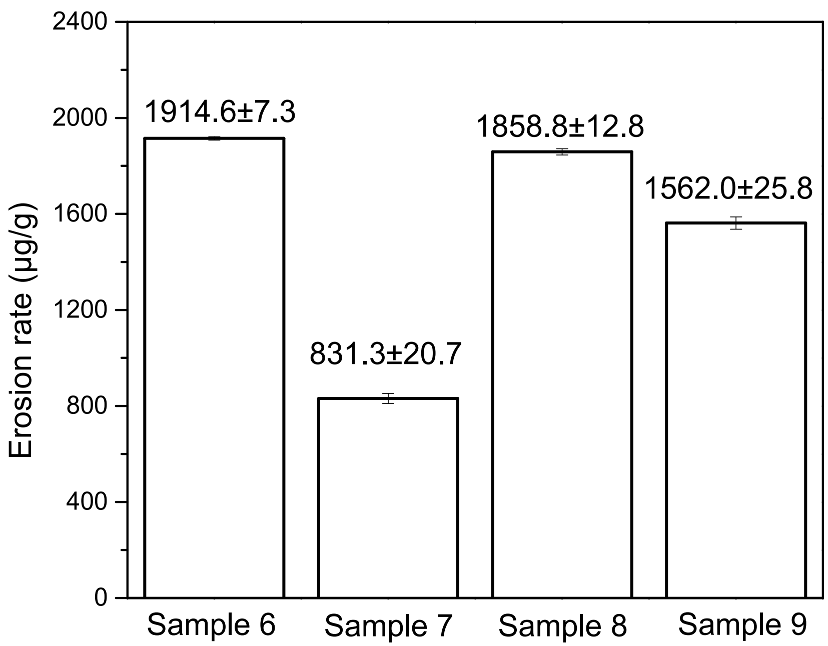
#6, Single layer $La_2Zr_2O_7$ *#7, Porous 8YSZ.* *#8, $La_2Zr_2O_7$ +Porous 8YSZ* *#9, $La_2Zr_2O_7$ +Dense 8YSZ*



Erosion rate & critical erosion velocity

Erosion rate describes the erosion resistance of TBC sample [1]:

$$R_{erosion} = \frac{W_{removed\ material}}{W_{impacting\ particles}}$$

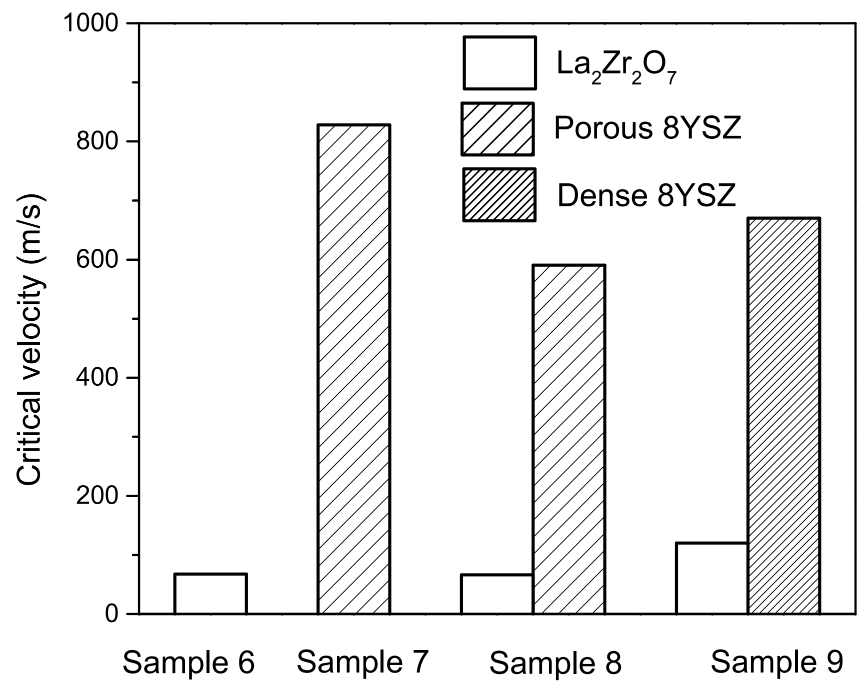


[1] D. Park, Int J Adv Manuf Technol, 23 (2004) 444-450.

Critical erosion velocity is used to express the critical condition to initiate cracks [2]:

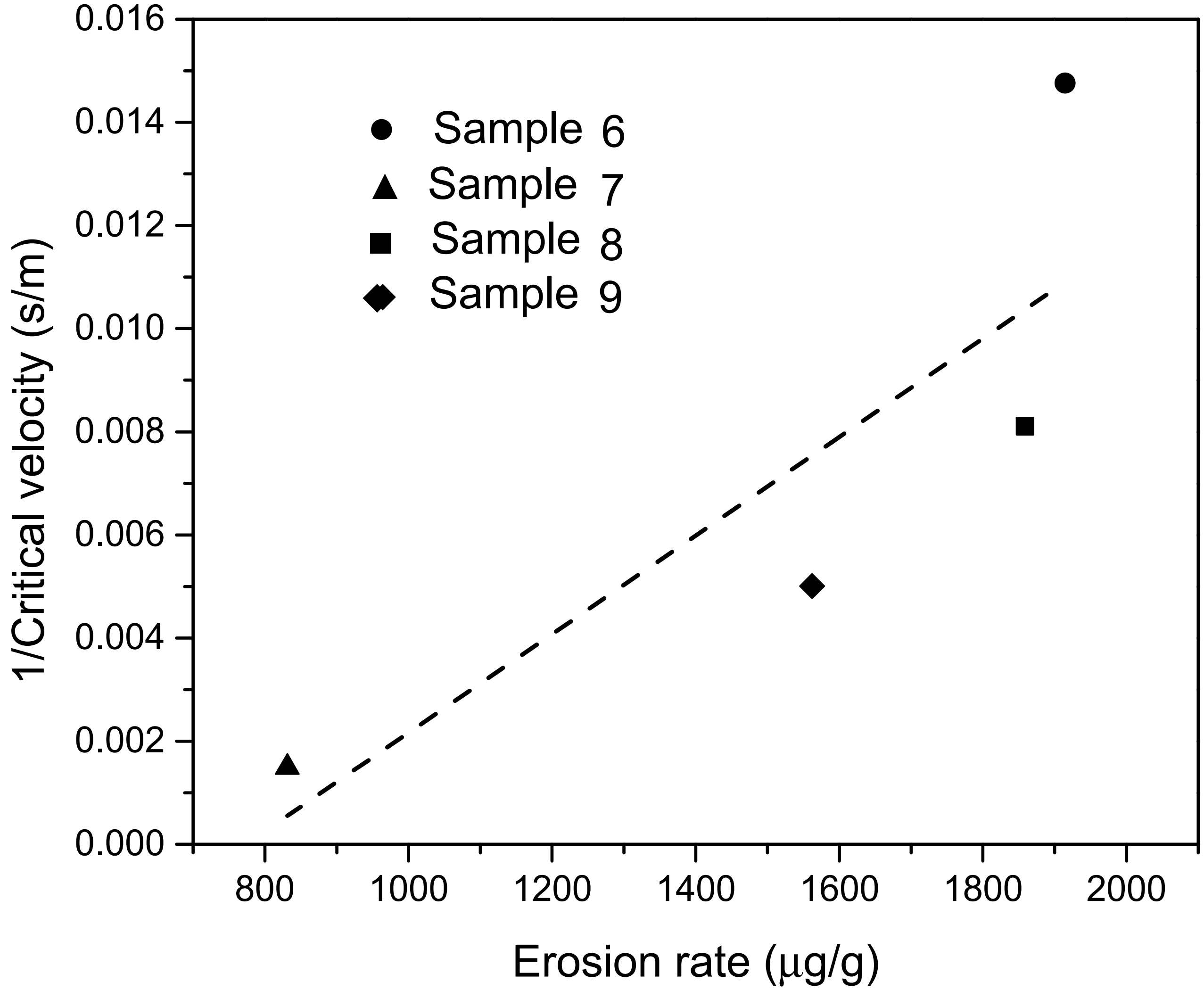
$$V_{crit} = 105 \frac{E^{3/4} K_{IC}^{3}}{H^{13/4} \rho^{1/2} R^{3/2}}$$

E: Young's modulus
H: hardness
K_{IC} :fracture toughness
ρ: density of erodent particle
R: particle radius



[2] R.G. Wellman, Wear, 256 (2004) 889-899.

Relationship between Vcrit and erosion rate



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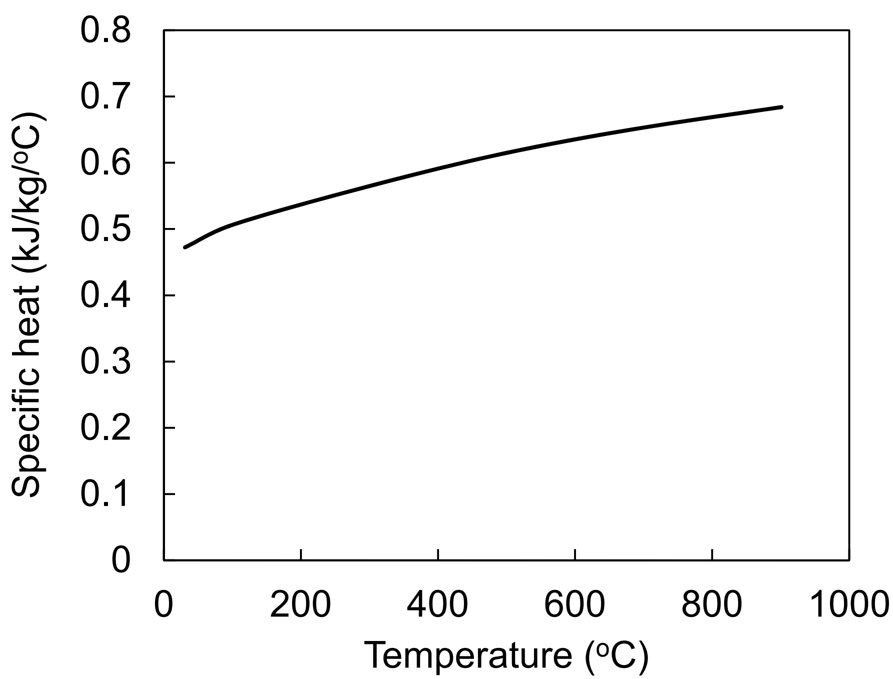
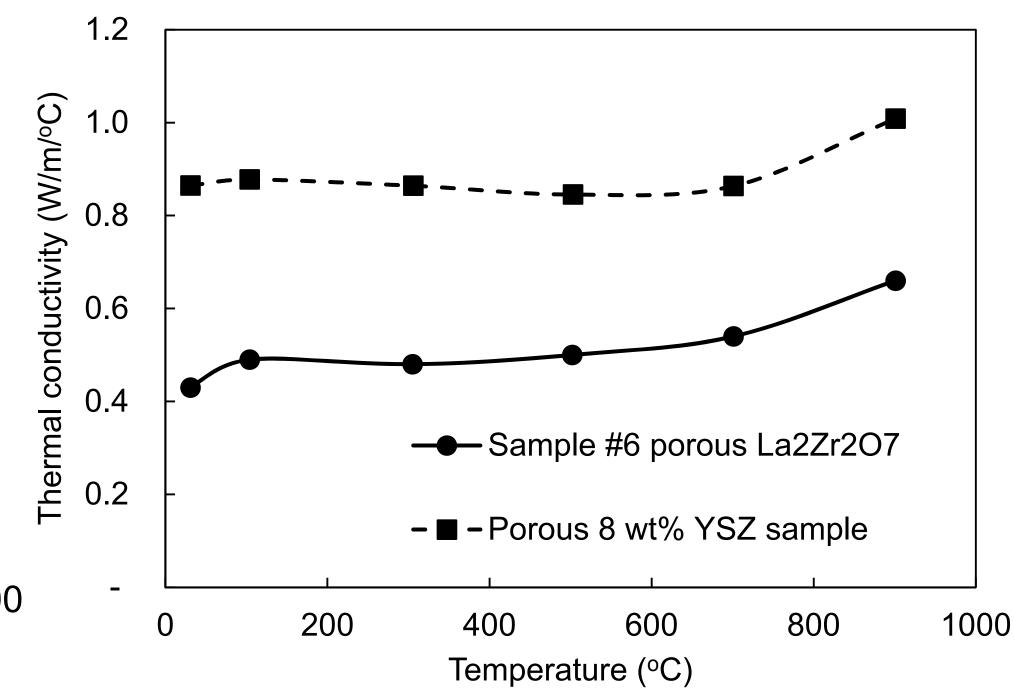
Thermal conductivity

Thermal conductivity is determined from thermal diffusivity D_{th}, specific heat capacity C_p, and measured density ρ:

$$k = D_{th} \cdot C_p \cdot \rho$$

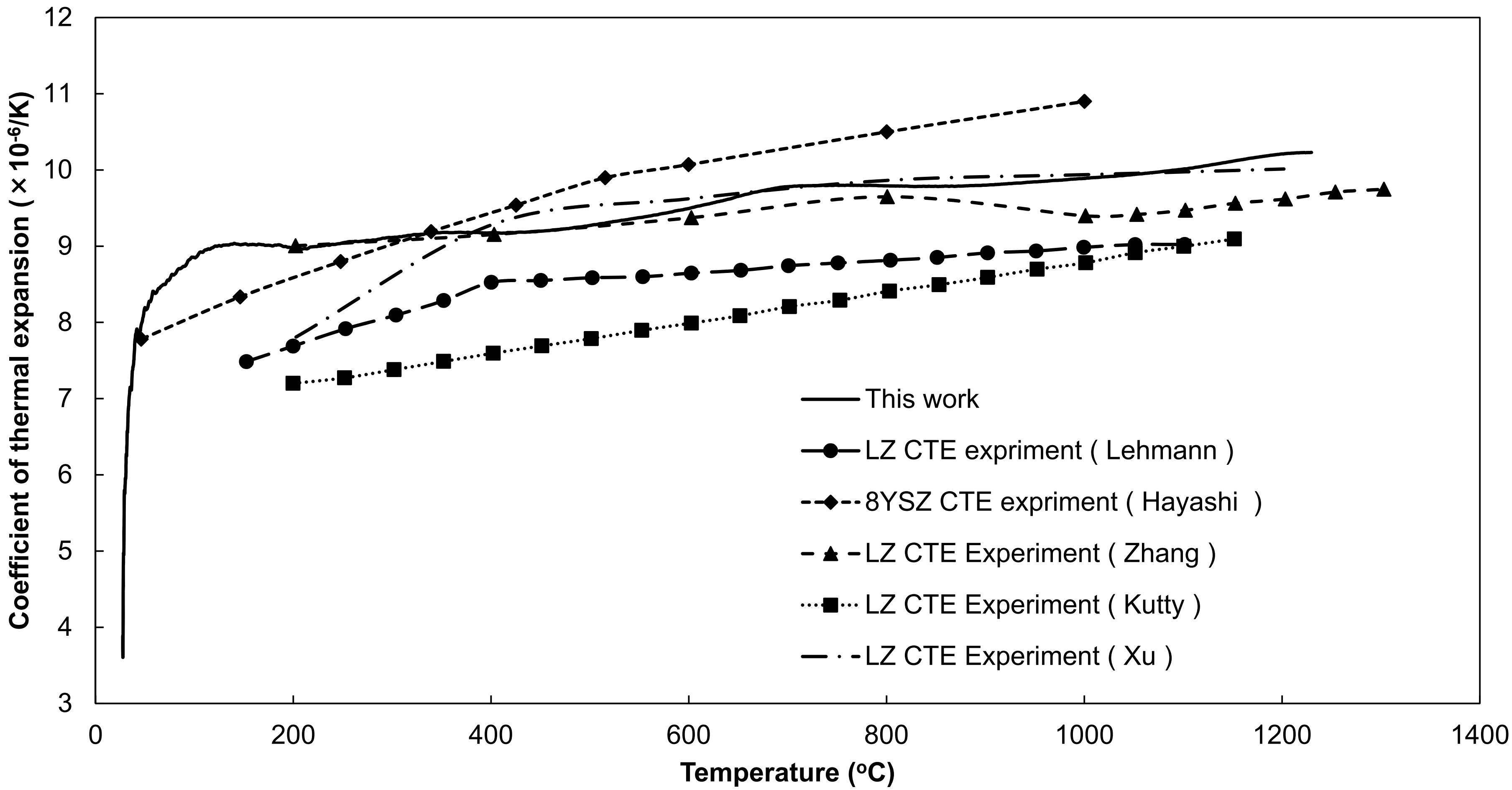
Thermal diffusivity is measured using laser flash diffusivity system (TA instrument DLF1200). Specific heat is measured by analytical method (TA instrument DLF1200)





Guo, *et al.*, Thermal properties, thermal shock and thermal cycling behavior of lanthanum zirconate based thermal barrier coatings, *Metallurgical and Materials Transactions E*, (DOI: 10.1007/s40553-016-0070-4)

Coefficient of thermal expansion (CTE)



CTE is measured using a BAEHR dilatometer from 25 to 1400 ^{o}C.

H. Lehmann, D. Pitzer, G. Pracht, R. Vassen, D. Stöver, Journal of the American Ceramic Society, 86 (2003) 1338-1344.
H. Hayashi, T. Saitou, N. Maruyama, H. Inaba, K. Kawamura, M. Mori, Solid State Ionics, 176 (2005) 613-619.

Guo, *et al.*, Thermal properties, thermal shock and thermal cycling behavior of lanthanum zirconate based thermal barrier coatings, *Metallurgical and Materials Transactions E*, (DOI: 10.1007/s40553-016-0070-4)

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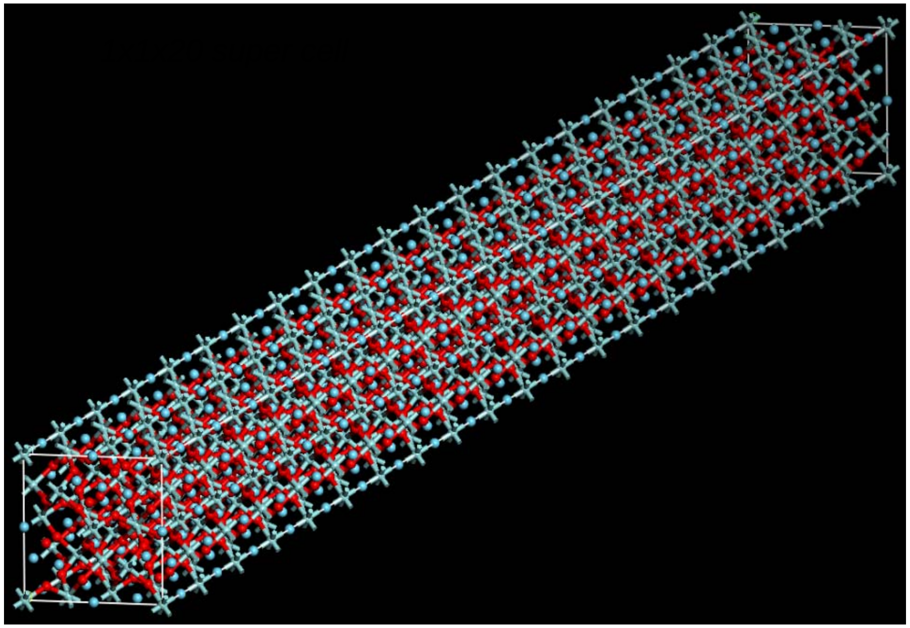
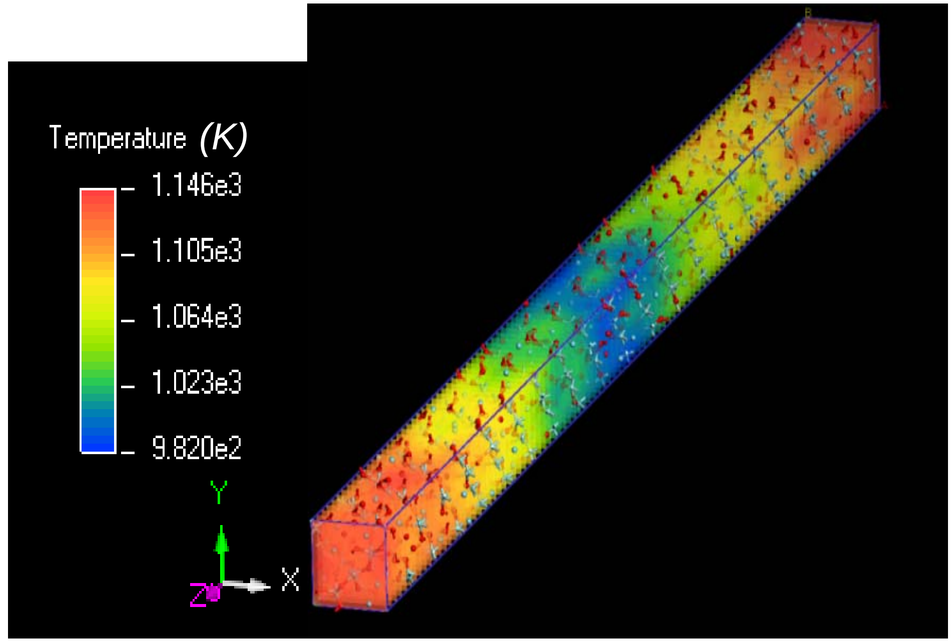
$La_2Zr_2O_7$ thermal conductivity calculation



Replicate 20 conventional cells along the heat flow direction to form a super cell



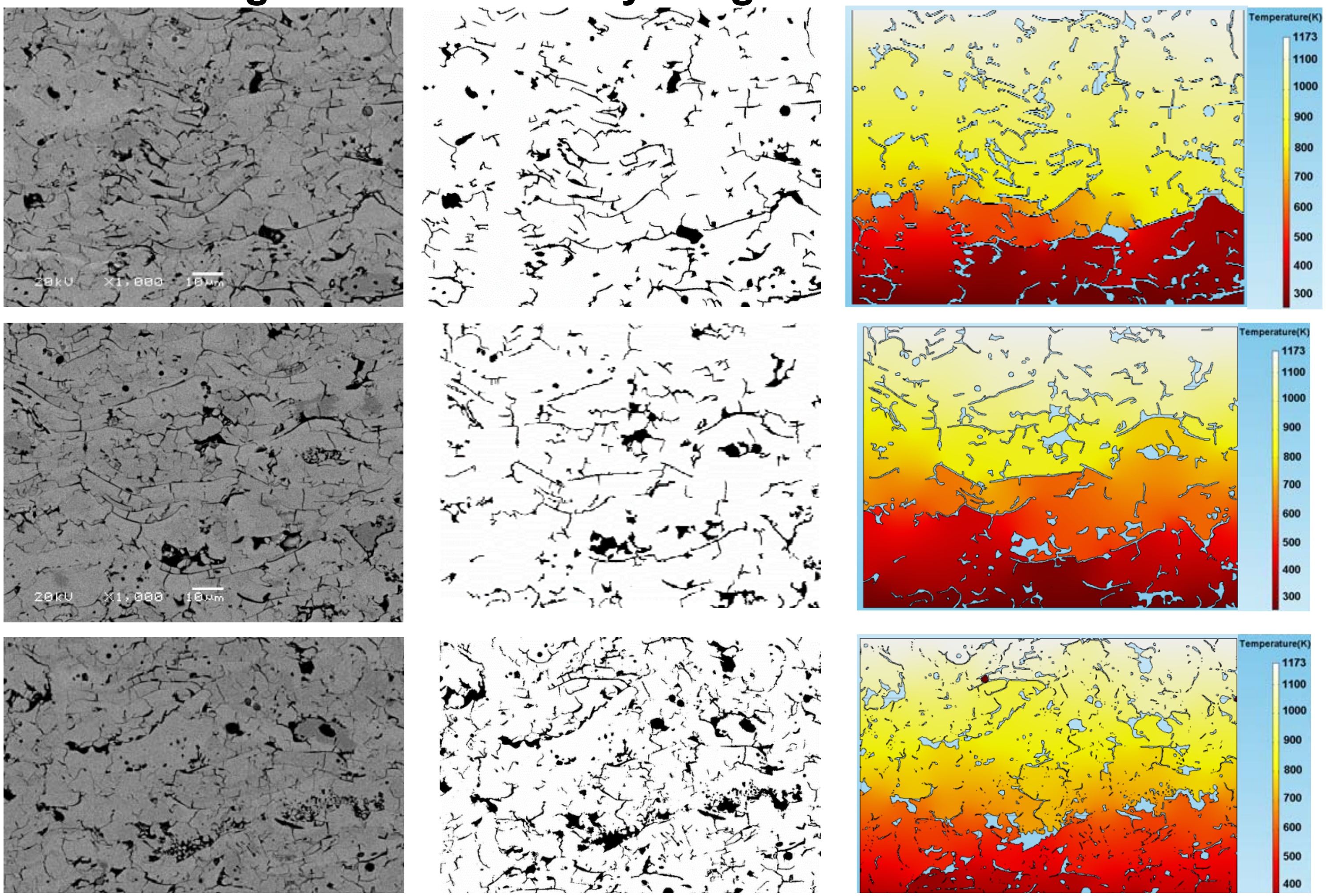
Calculated temperature contour based on Fourier's law $k = -\overrightarrow{q''}/\vec{\nabla}T$

The calculated thermal conductivity is 1.2 W/m/K at the temperature of 1000 ^{o}C, which is reasonably in agreement with the experimentally measured thermal conductivity ~1.5 W/m/K [1].

Guo, *et al*., Image-Based Multi-Scale Simulation and Experimental Validation of Thermal Conductivity of Lanthanum Zirconate, *International Journal of Heat and Mass Transfer*, (doi:10.1016/j.ijheatmasstransfer.2016.04.067)

Imaged based FEM calculation of thermal conductivity of $La_2Zr_2O_7$ TBC

SEM image **Binary image** **FEM model**



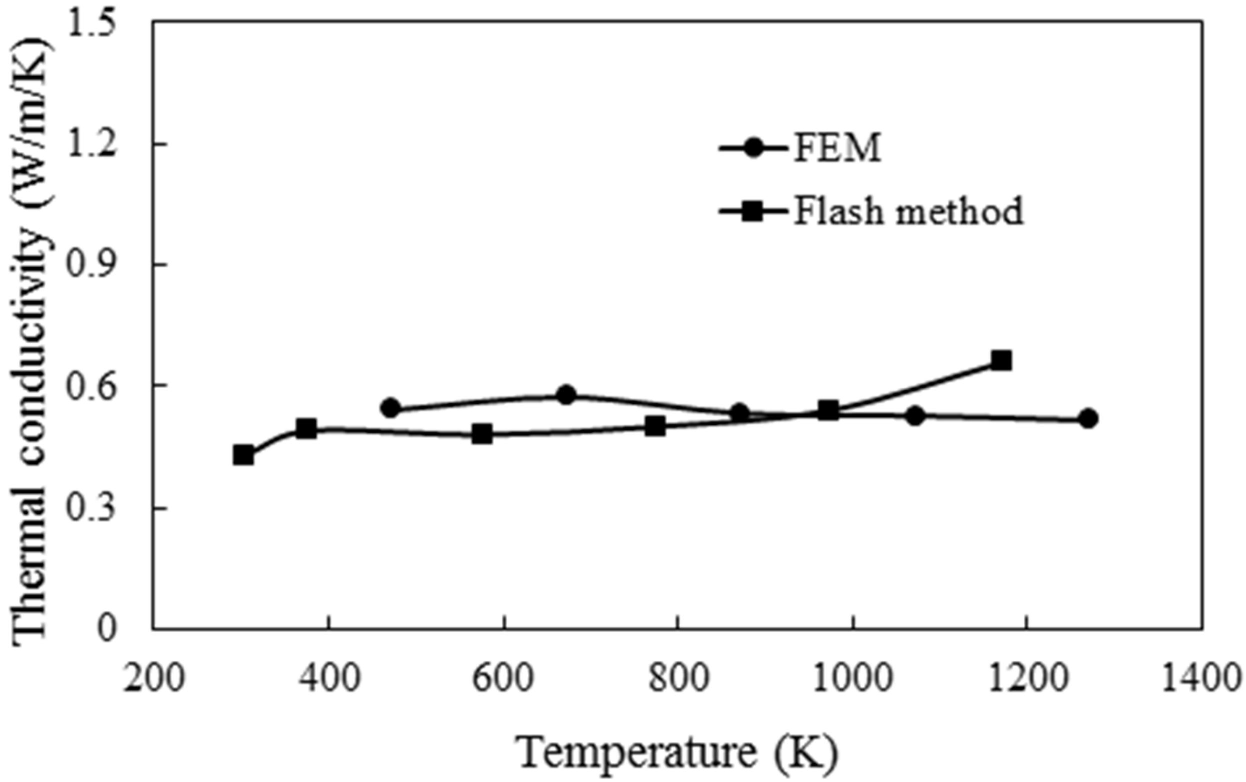
k=0.538 W/m/K

k=0.550 W/m/K

k=0.723 W/m/K

Guo, *et al*., Image-Based Multi-Scale Simulation and Experimental Validation of Thermal Conductivity of Lanthanum Zirconate, *International Journal of Heat and Mass Transfer*, (doi:10.1016/j.ijheatmasstransfer.2016.04.067)

Imaged based FEM calculation of thermal conductivity of $La_2Zr_2O_7$ coating



Calculated thermal conductivity ~0.60 W/m-K, in good agreement with experimental data.

Guo, *et al*., Image-Based Multi-Scale Simulation and Experimental Validation of Thermal Conductivity of Lanthanum Zirconate, *International Journal of Heat and Mass Transfer*, (doi:10.1016/j.ijheatmasstransfer.2016.04.067)

Mapping thermal conductivity & heat capacity

Sample information

TBC:

Material: $La_2Zr_2O_7$

Thickness: ~600μm (this is used in calculation)

Density: 90.55% dense, dense density=6 g/cc, so density ρ = 5.478 g/cc

Specific heat: c = 0.54 J/g-K @1000C

Substrate (following are room temperature properties obtained from matweb):

Material: Haynes 188

Density: ρ = 8.98 g/cc

Thermal conductivity: k = 10.4 W/m-K,

Specific heat: c = 0.403 J/g-K, (therefore, ρc = 3.62 J/cm^3-K)

Thickness used in calculation: L = 4 mm (may have a small effect to results)

Test condition

Flash thermal imaging test with one flash lamp

Imaging speed: 994 Hz; imaging duration: 3 seconds

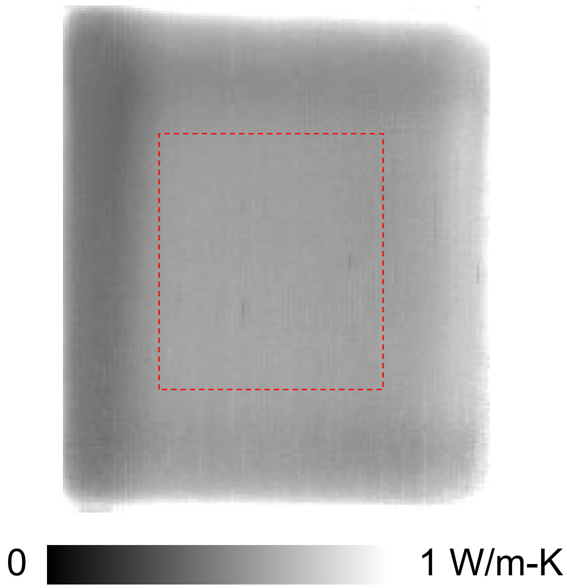
Thermal conductivity and heat capacity map

credit:
Jiangan Sun
@ ANL

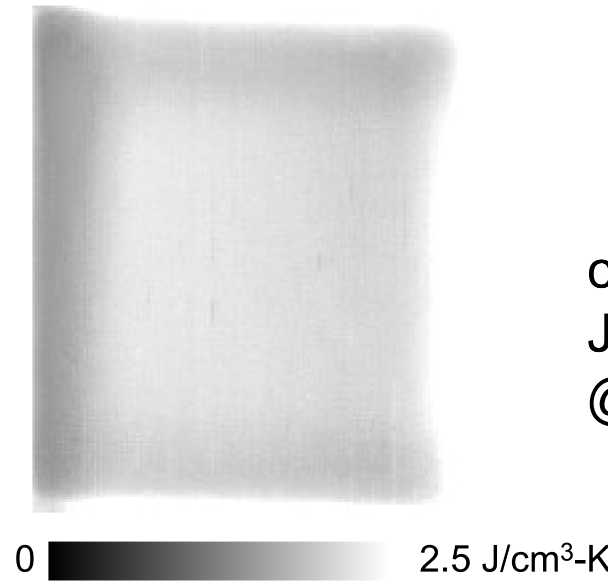
TBC is 90.55% dense (ρ=5.478g/cc), with a nominal thickness of 600μm
Indentation marks are from previous study

Mapping TBC thermal properties

Thermal conductivity *k* image



Heat capacity ρc image



credit:
Jiangan Sun
@ ANL

Predicted average TBC properties (within red rectangular area):

k = 0.55 W/m-K, ρc = 2.16 J/cm^3-K

- These results were based on a TBC thickness of 600 μm
- TBC specific heat @RT: c = 0.393 J/g-K; predicted TBC density is: ρ=ρc/c=2.16/0.393=5.5 g/cc

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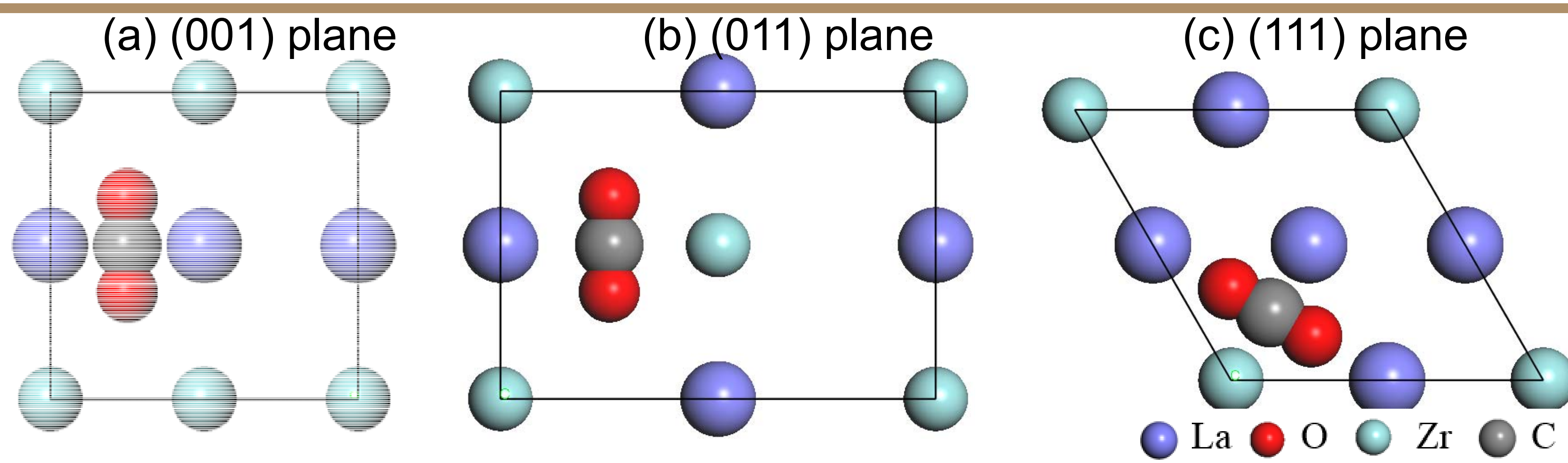
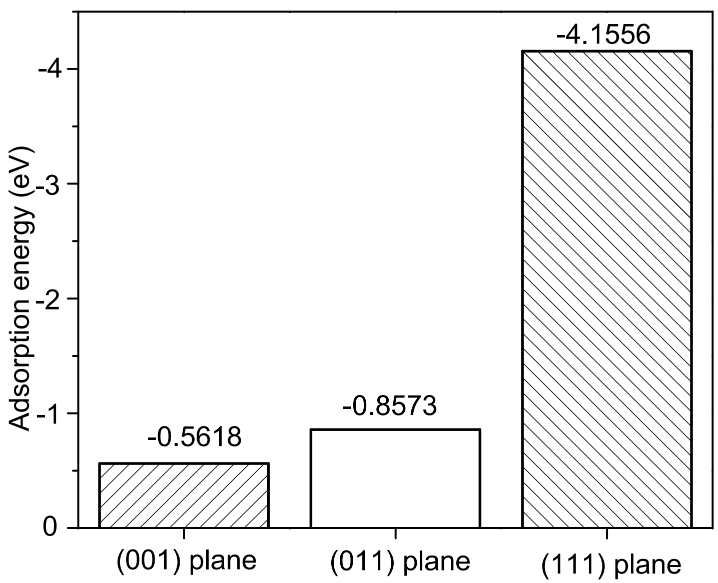
CO_2 adsorption on coating surfaces



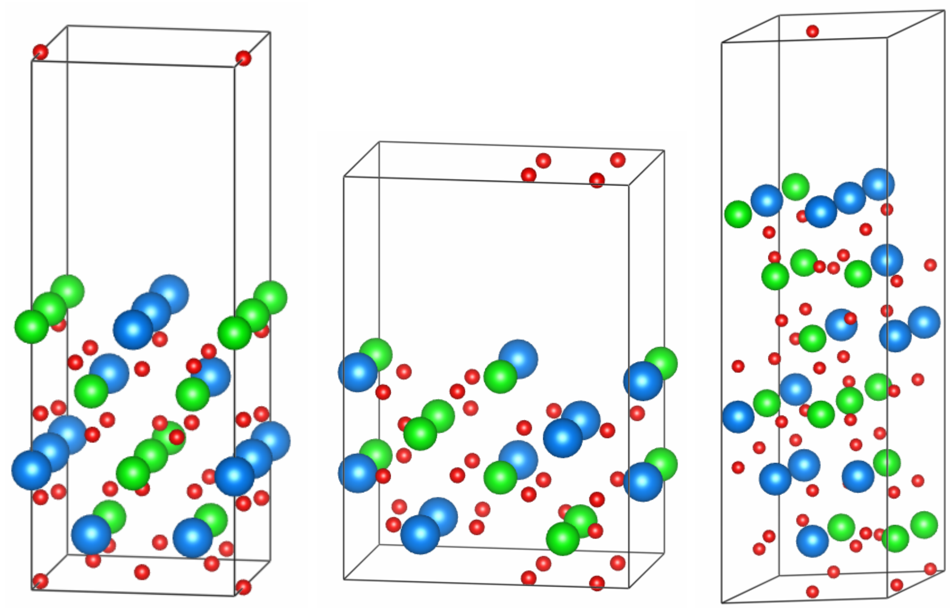
Top view of CO_2 adsorption sites on $La_2Zr_2O_7$ planes. Only $La_2Zr_2O_7$ top layer is shown



CO_2 is prone to be adsorbed on (111) plane, when the adsorption occurs in the bridge sites between La atom and Zr atom.

- Guo, *et al.*, Carbon dioxide adsorption on lanthanum zirconate nanostructured coating surface: a DFT study, *Adsorption*, 22(2), pp 159-163, (2016)

O_2 adsorption on coating surfaces


(a) (b) (c)

Computational slab models of various $La_2Zr_2O_7$ planes: (a) (001) plane, (b) (011) plane, and (c) (111) plane. The blue, green, and red balls indicate La atoms, Zr atoms, and O atoms, respectively.

$La_2Zr_2O_7$ plane	A: bridge position (La-Zr) (eV)	B: 4-fold position (eV)	C: 3-fold-FCC position (eV)	D: 3-fold-HCP position (eV)
(001)	-3.5127	-5.1148	-	-
(011)	-5.0240	-1.3080	-	-
(111)	-3.5795	-	-5.5302	-3.8070

The adsorption energies are exothermic. The lowest adsorption energy site is the 3-fold-FCC on (111) plane, confirmed by Bader charge transfer analyses.

- Guo, *et al.*, First Principles Study of Nanoscale Mechanism of Oxygen Adsorption on Lanthanum Zirconate Surfaces, *Physica E*, (doi:10.1016/j.physe.2016.04.012)

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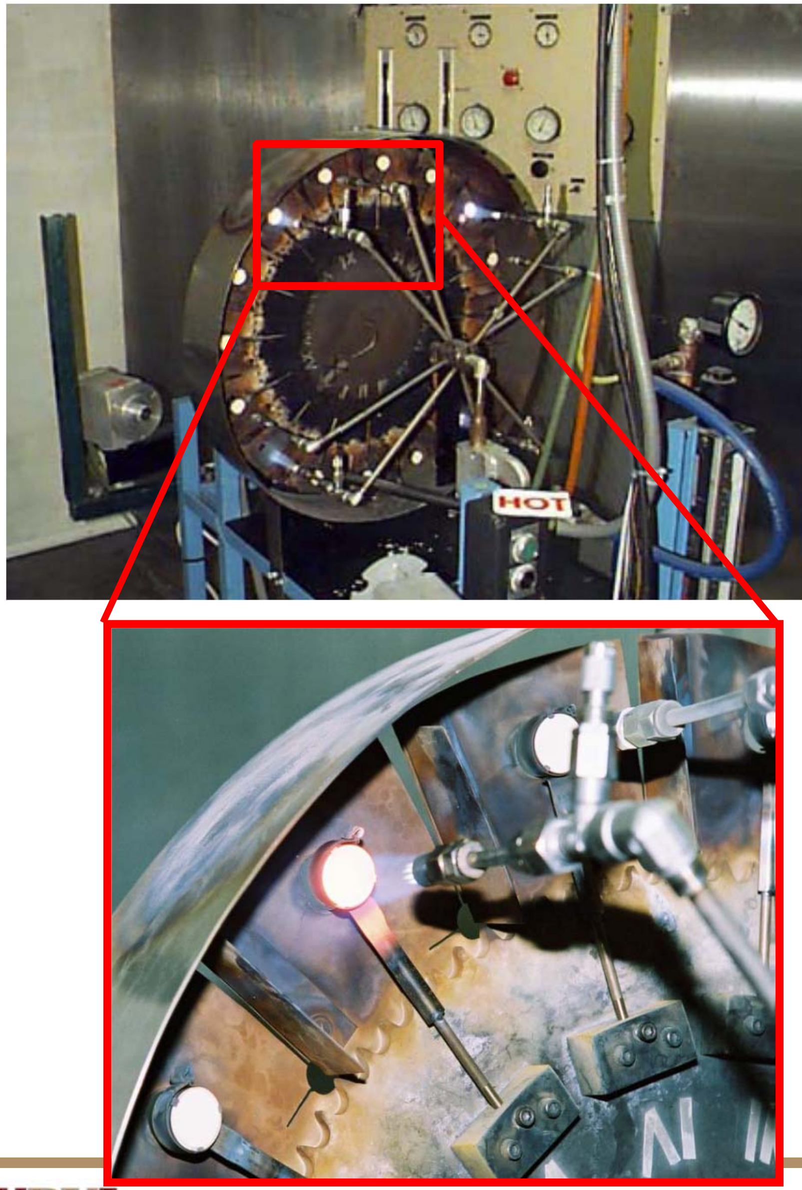
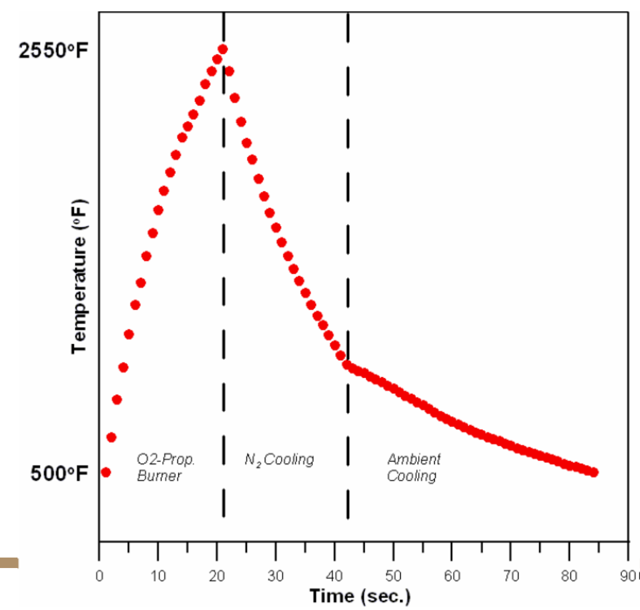
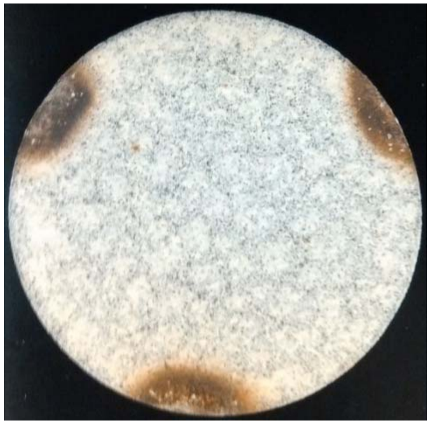
Jet engine thermal shock tests (JETS)



- Jet engine thermal shock (JETS) tests are conducted to investigate the thermal cycling performance.
- TBC samples are heated to 2250 °F (1232.2 °C) at the center for 20 s, and then cooled by compressed N_2 cooling for 20 s, and then ambient cooling for 40 s.
- Temperatures are measured by thermal couple and pyrometer.



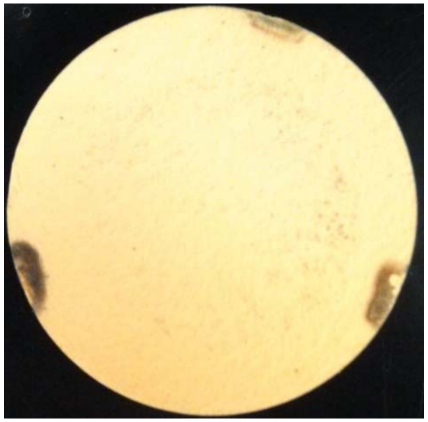
Jet engine thermal shock test (JETS) results



Single layer $La_2Zr_2O_7$

Porous 8YSZ+ $La_2Zr_2O_7$

Dense 8YSZ+ $La_2Zr_2O_7$

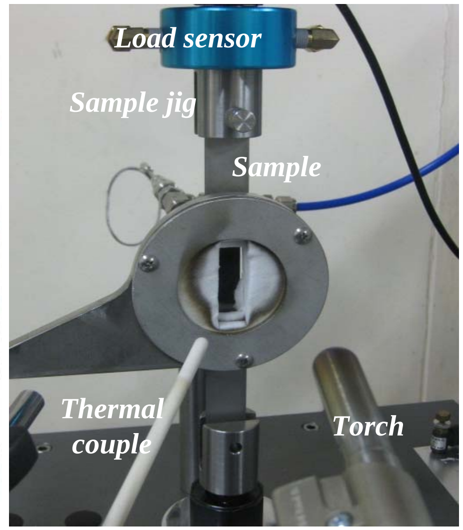


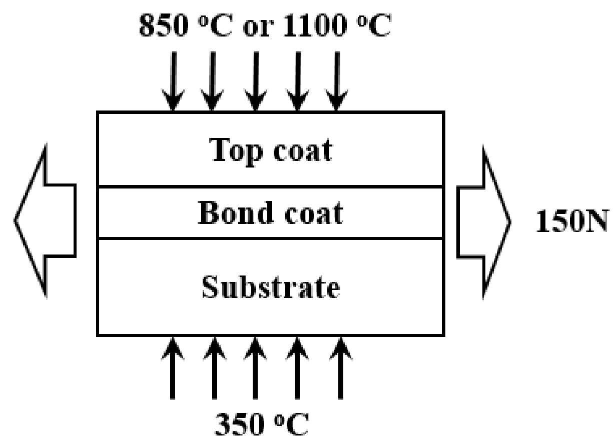
Porous 8YSZ

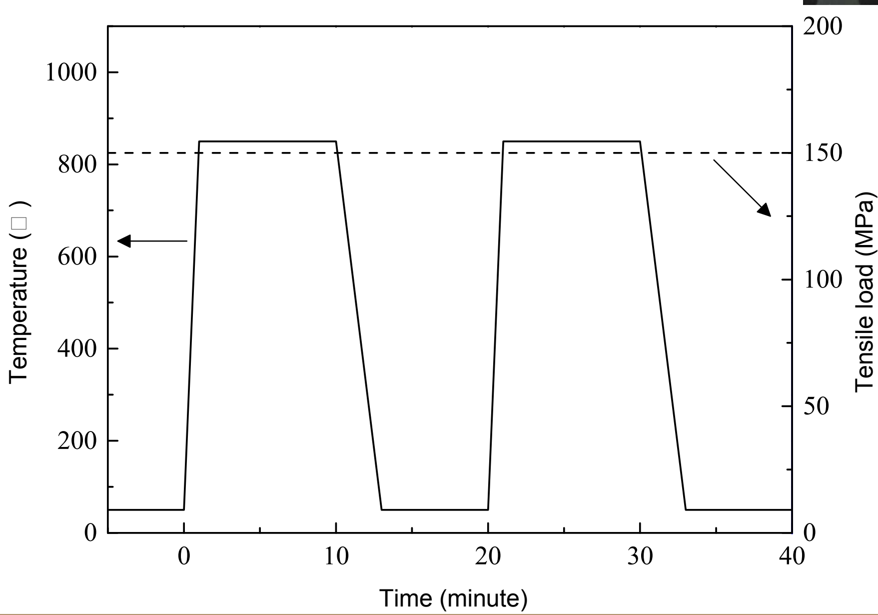
	Single-layer $La_2Zr_2O_7$	Porous 8YSZ + $La_2Zr_2O_7$	Dense 8YSZ + $La_2Zr_2O_7$	Single-layer porous 8YSZ
Number of cycles	25	> 2000	885	> 2000
Failure status	Complete delaminated	Edge delaminated	Complete delaminated	Intact

Guo, *et al.*, Thermal properties, thermal shock and thermal cycling behavior of lanthanum zirconate based thermal barrier coatings, *Metallurgical and Materials Transactions E*, (DOI: 10.1007/s40553-016-0070-4)

Thermal gradient mechanical fatigue (TGMF)







At 850 °C

Sample	Test cycle
SCL porous 8YSZ	1200
DCL porous 8YSZ + $La_2Zr_2O_7$	220
DCL dense 8YSZ + $La_2Zr_2O_7$	50

At 1100 °C

Sample	Test cycle
DCL porous 8YSZ + $La_2Zr_2O_7$	38
DCL dense 8YSZ + $La_2Zr_2O_7$	49

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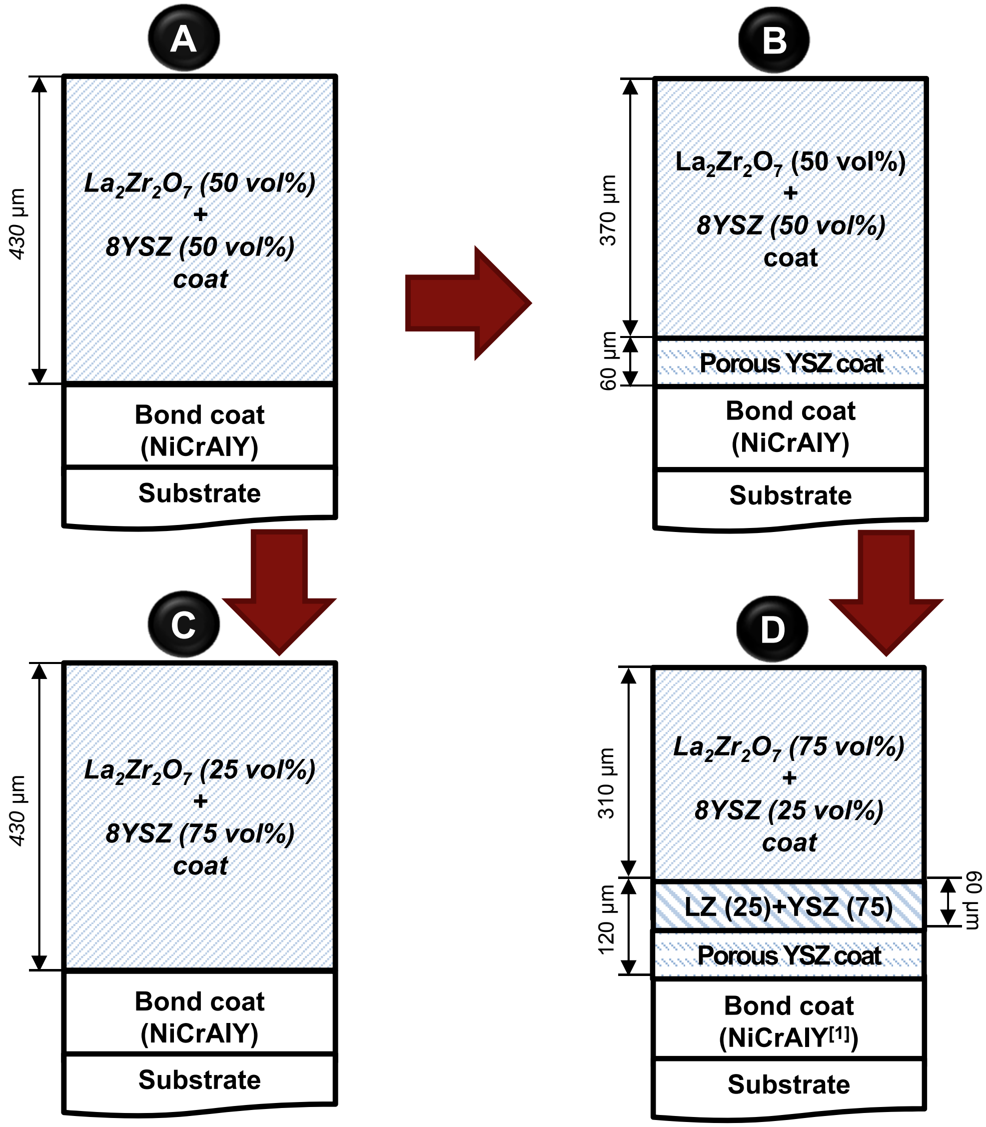
Composite coatings with buffer layers



In order to improve the thermal durability in thermal cycling tests, new composite top coats are proposed:

thermal conductivity + matching CTEs

Introducing 1st buffer layer:

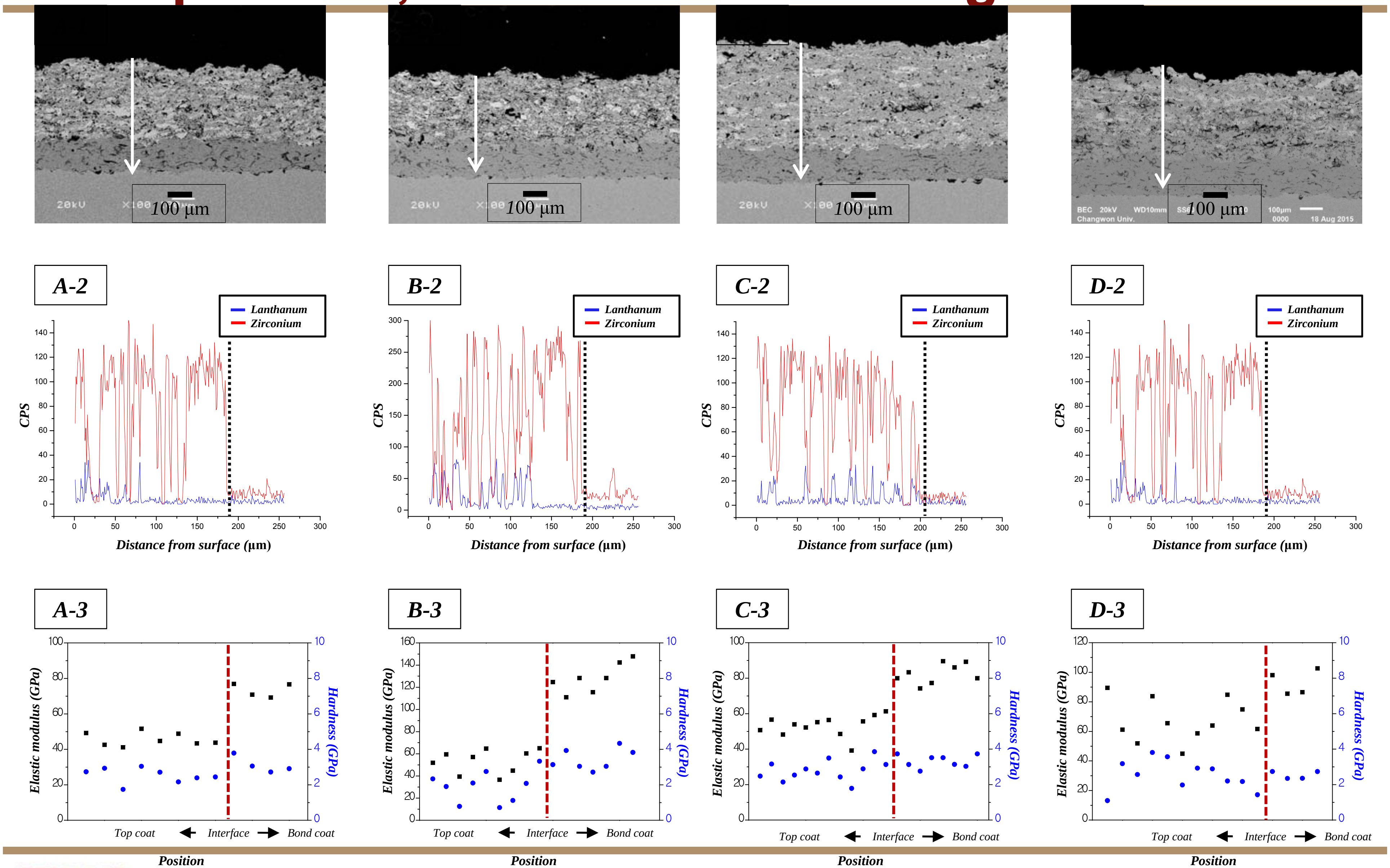
Increasing strain compliance + Decreasing CTEs mismatch

2nd buffer layer:

Further decrease CTEs mismatch

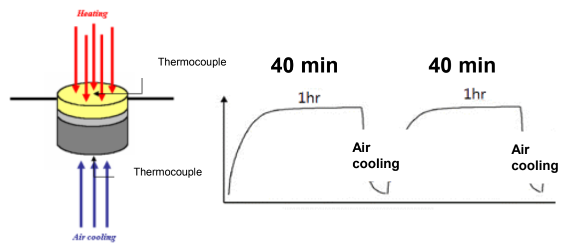
- Song, *et al.*, Microstructure design for blended feedstock and its thermal durability in lanthanum zirconate based thermal barrier coatings, *ICMCTF 2016*

As-coated composite coatings: microstructure, composition, hardness and Young's modulus



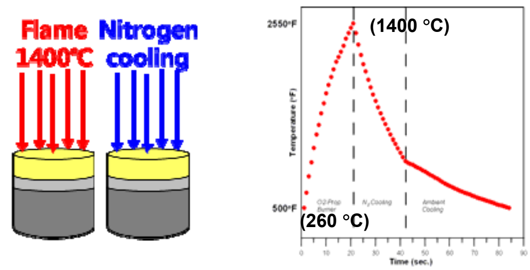
Thermal durability tests

Furnace cycling thermal fatigue (FCTF)



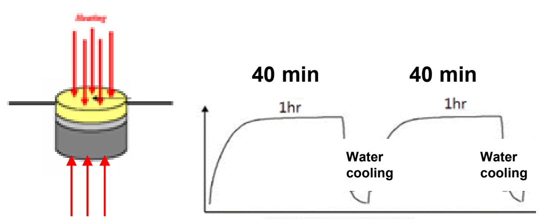
- Top surface temperature : ~ 1100 ℃
- Bottom surface temperature : ~ 950 ℃
- Heating time : 40 min
- Cooling type : Air & gas cooling

Jet engine thermal shock (JETS)



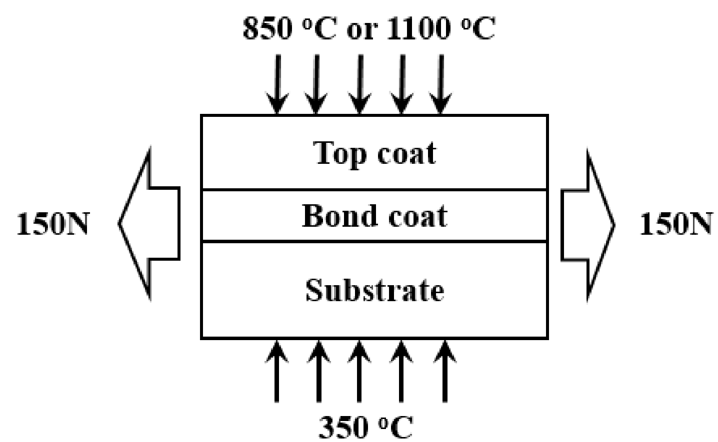
- Flame temperature : ~1400 ℃
- Holding time : 20 sec
- Cooling time : 20 sec
- Cooling type : Nitrogen quenching

Thermal shock (TS)



- Heating temperature : ~ 1100 °C
- Heating time : 40 min
- Cooling type : Water quenching (30 °C)

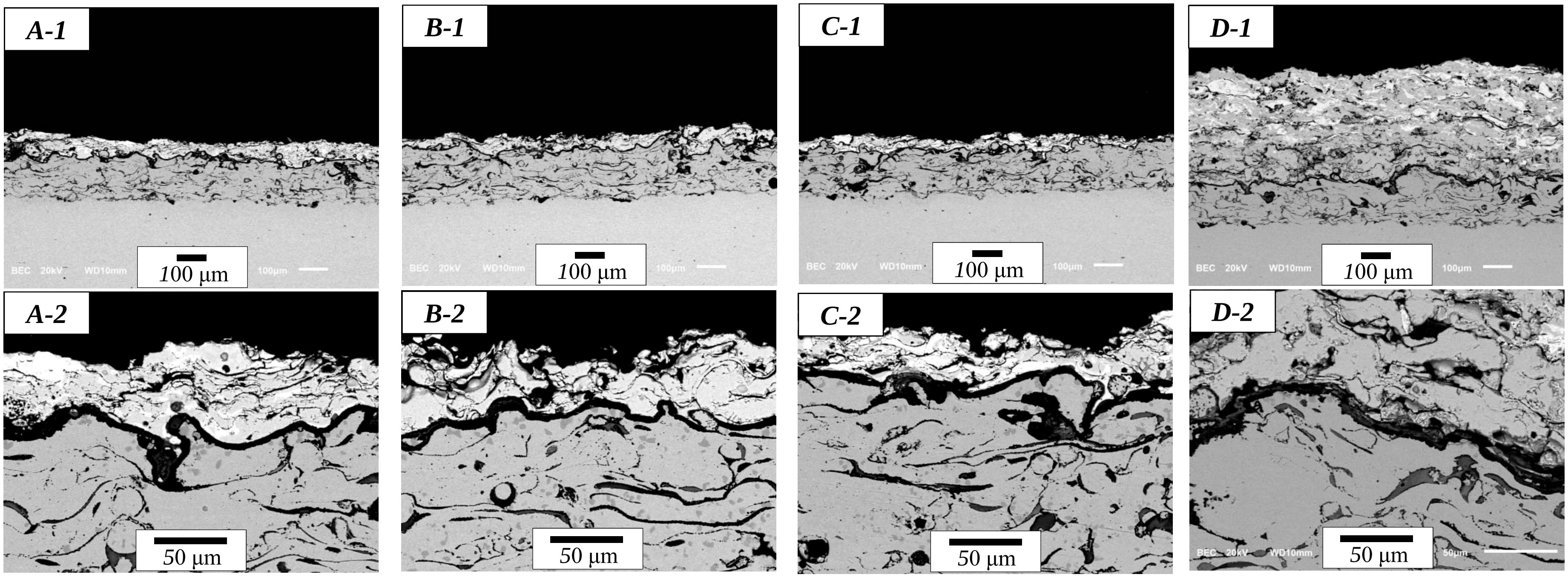
Thermal gradient mechanical fatigue (TGMF)



Thermal durability of composite coatings

Sample species	FCTF test/Status	TS test/Status	JETS test/Status
(A) SLC TBC (50% LZ : 50 % YSZ in volume)	540 cycles/ Fully delaminated	10 cycles/ Fully delaminated	70 cycles/ Fully delaminated
(B) DLC TBC (50% LZ : 50 % YSZ in volume) with single buffer layer	768 cycles/ Fully delaminated	29 cycles/ Fully delaminated	2000 cycles/ Sound condition
(C) SLC TBC (25% LZ : 75 % YSZ in volume)	936 cycles/ Fully delaminated	14 cycles/ Fully delaminated	1022 cycle/ Fully delaminated
(D) DLC TBC (50% LZ : 50 % YSZ in volume) with double buffer layers	1143 cycles/ Sound condition	54 cycles/ Partially delaminated	2000 cycles/ Sound condition

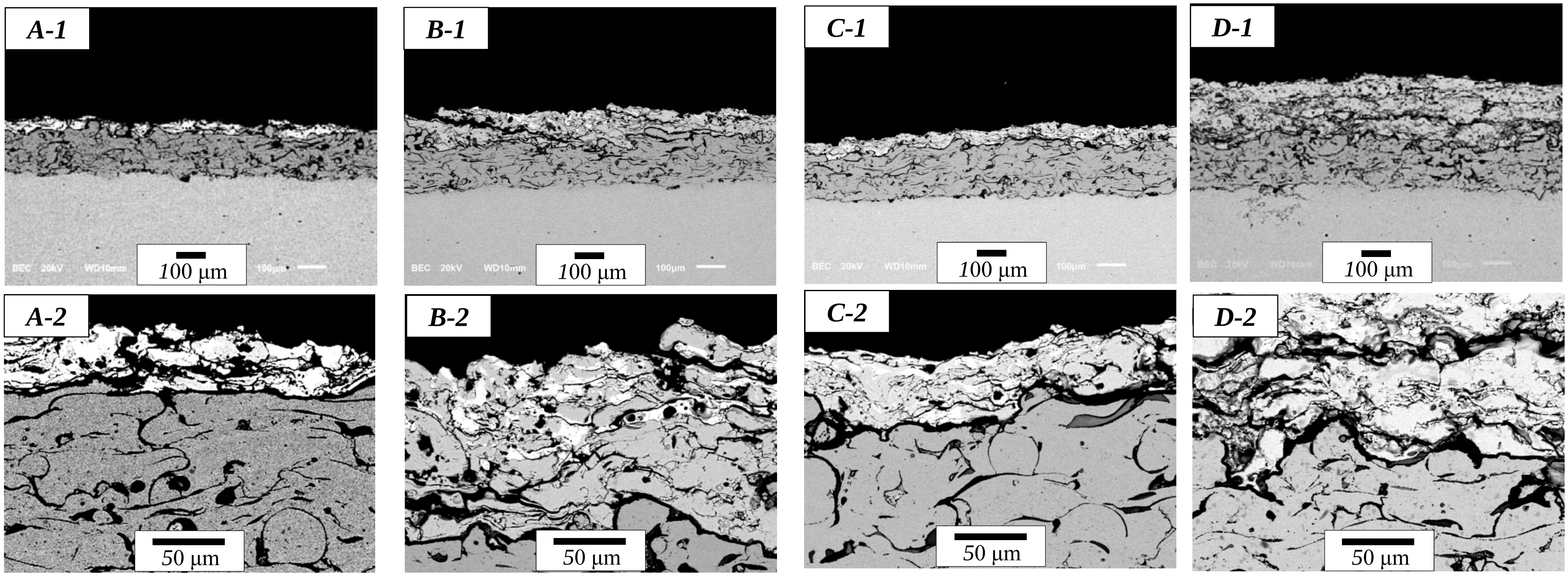
Cross-sectional view after furnace cycling thermal fatigue (FCTF) test



- Delamination within top coat and/or the interface between the top and bond coats in A, B, and C.
- Thermally grown oxide (TGO) layer at interface between the top and bond coats in all samples
- Spinel (Cr_2O_3, $NiAl_2O_4$) in the TGO in D due to longer thermal exposure.

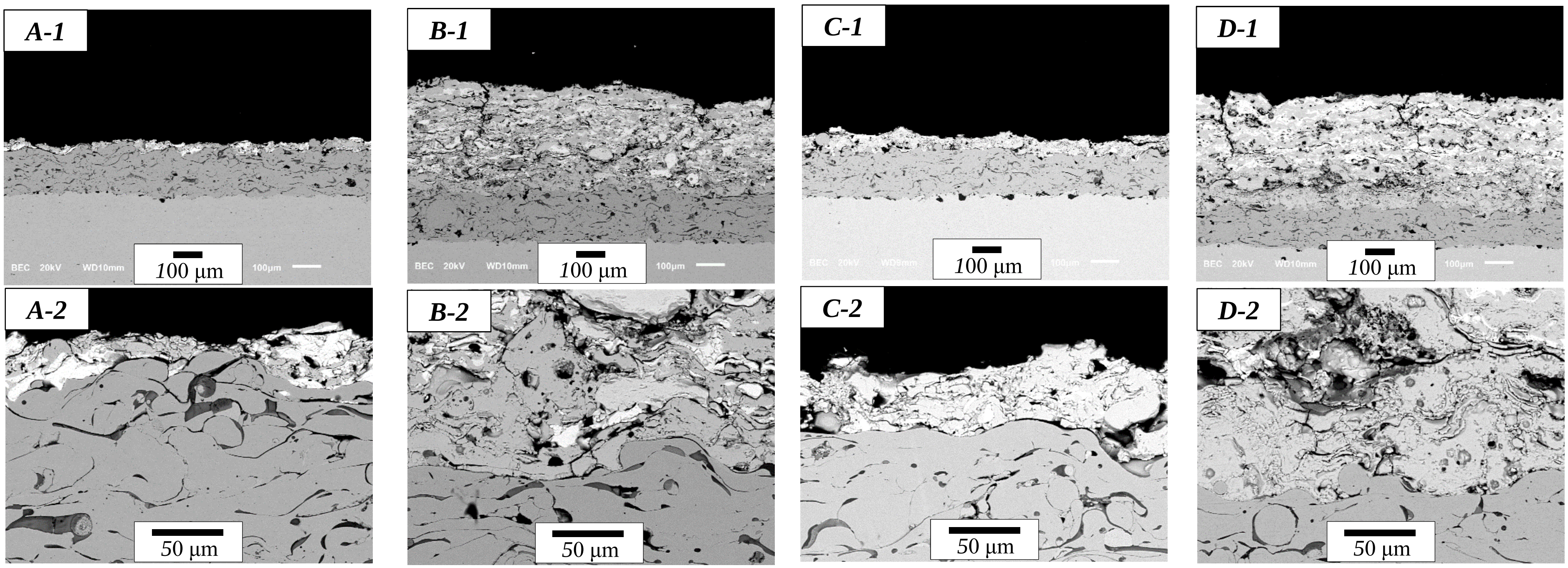
Song, *et al.*, Microstructure design for blended feedstock and its thermal durability in lanthanum zirconate based thermal barrier coatings, *ICMCTF 2016*

Cross-sectional view after thermal shock (TS) test



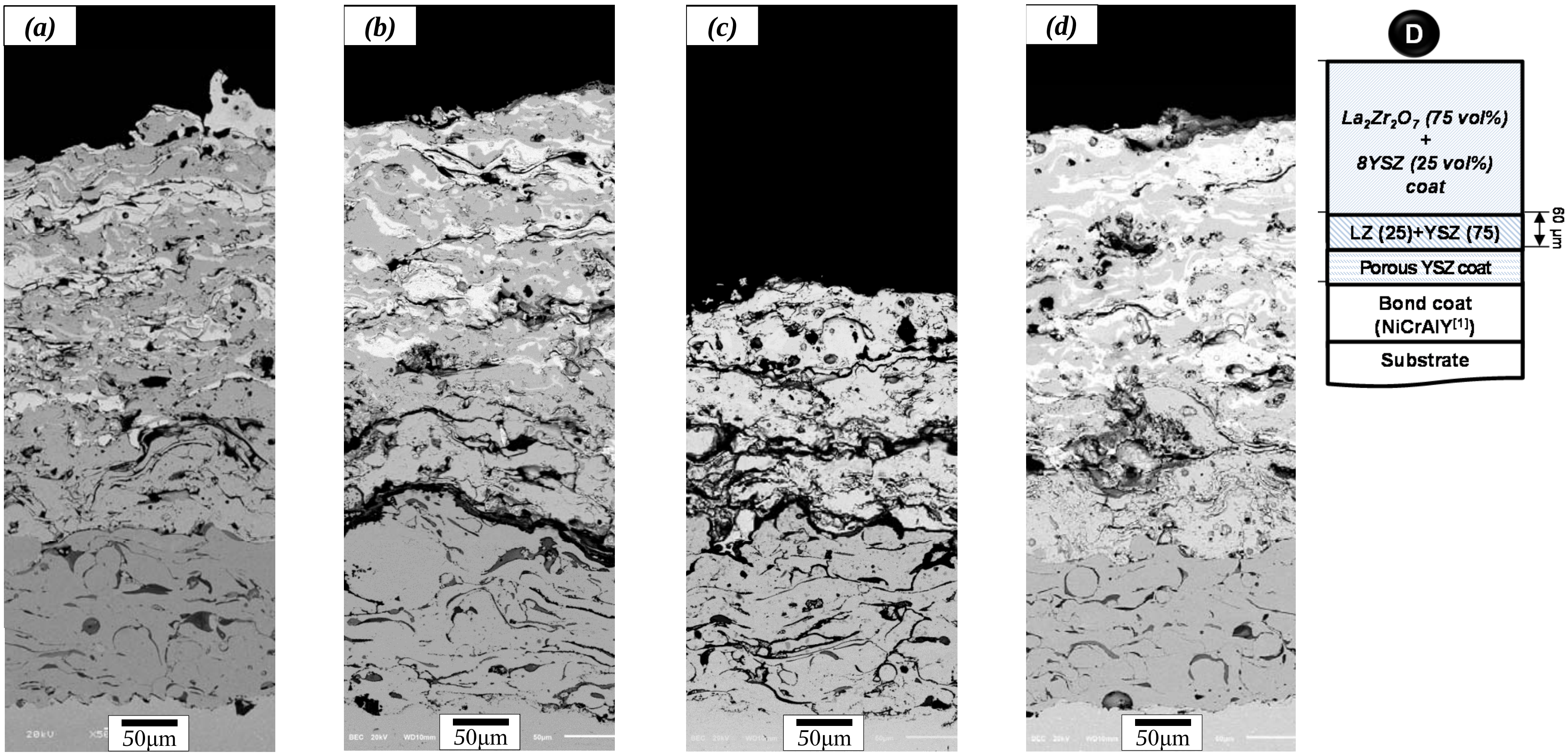
- In TS tests, A and C were delaminated less than 15 cycles, showing a thinner TGO layer than those in FCTF tests, due to CTE difference and low fracture toughness of LZ.
- B (survived 29 cycles, fully delaminated) and D (54 cycles, partially delaminated).

Cross-sectional view after jet engine thermal shock (JETS) test



- A and C survived 70 and 1022 cycles, respectively.
- B and D survived 2000 cycles, showing a superior stability. (a) B and D showed vertical cracks during JETS test; (b) buffer layer(s); and (c) composite coats.

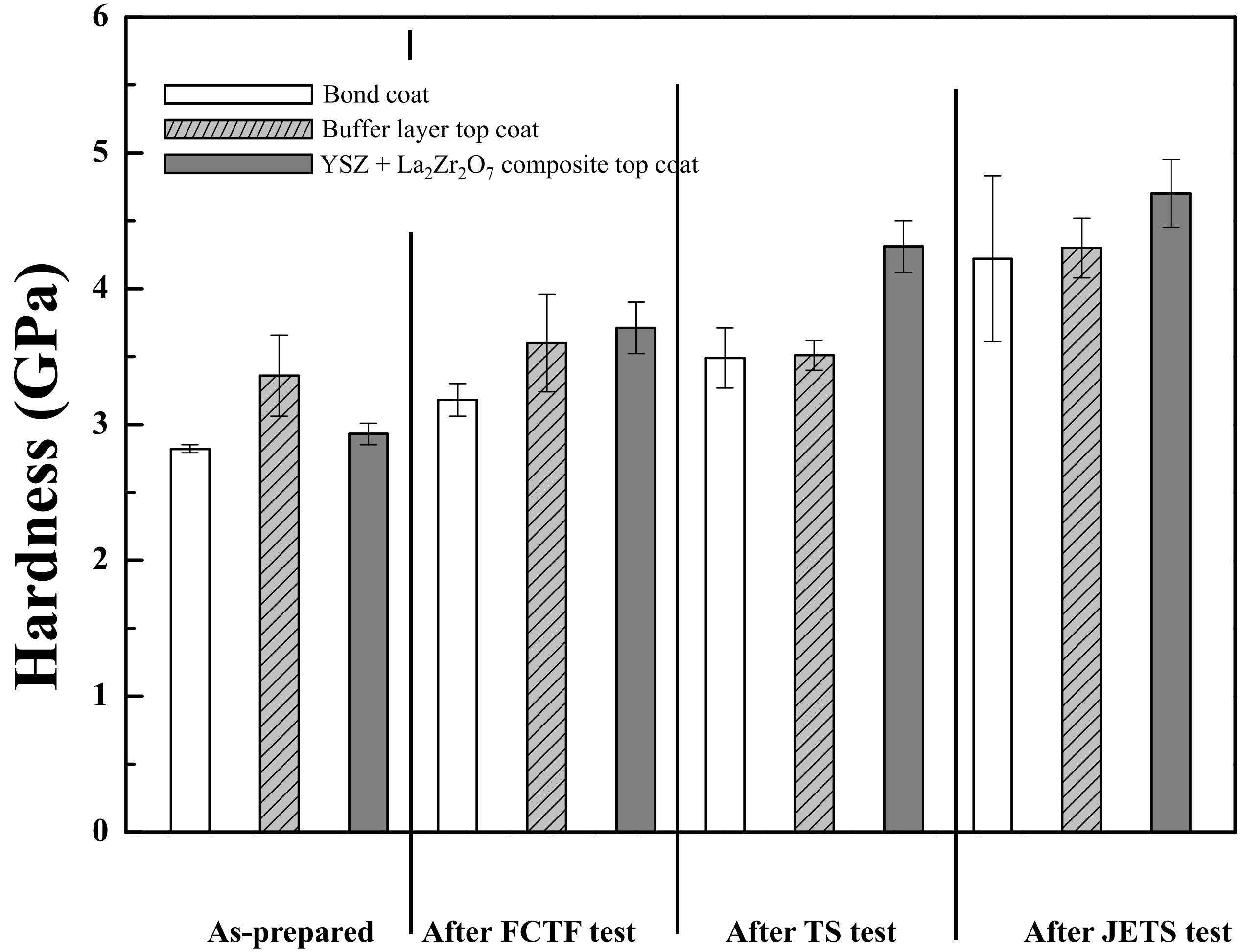
Composite coating with double buffer layers

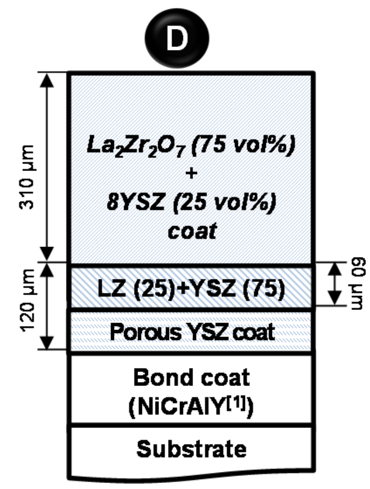


(a) as-coated (b) after FCTF (c) after TS (d) after JETS

- Song, *et al.*, Microstructure design for blended feedstock and its thermal durability in lanthanum zirconate based thermal barrier coatings, *ICMCTF 2016*

Vicker's hardness of composite coating with double buffer layers





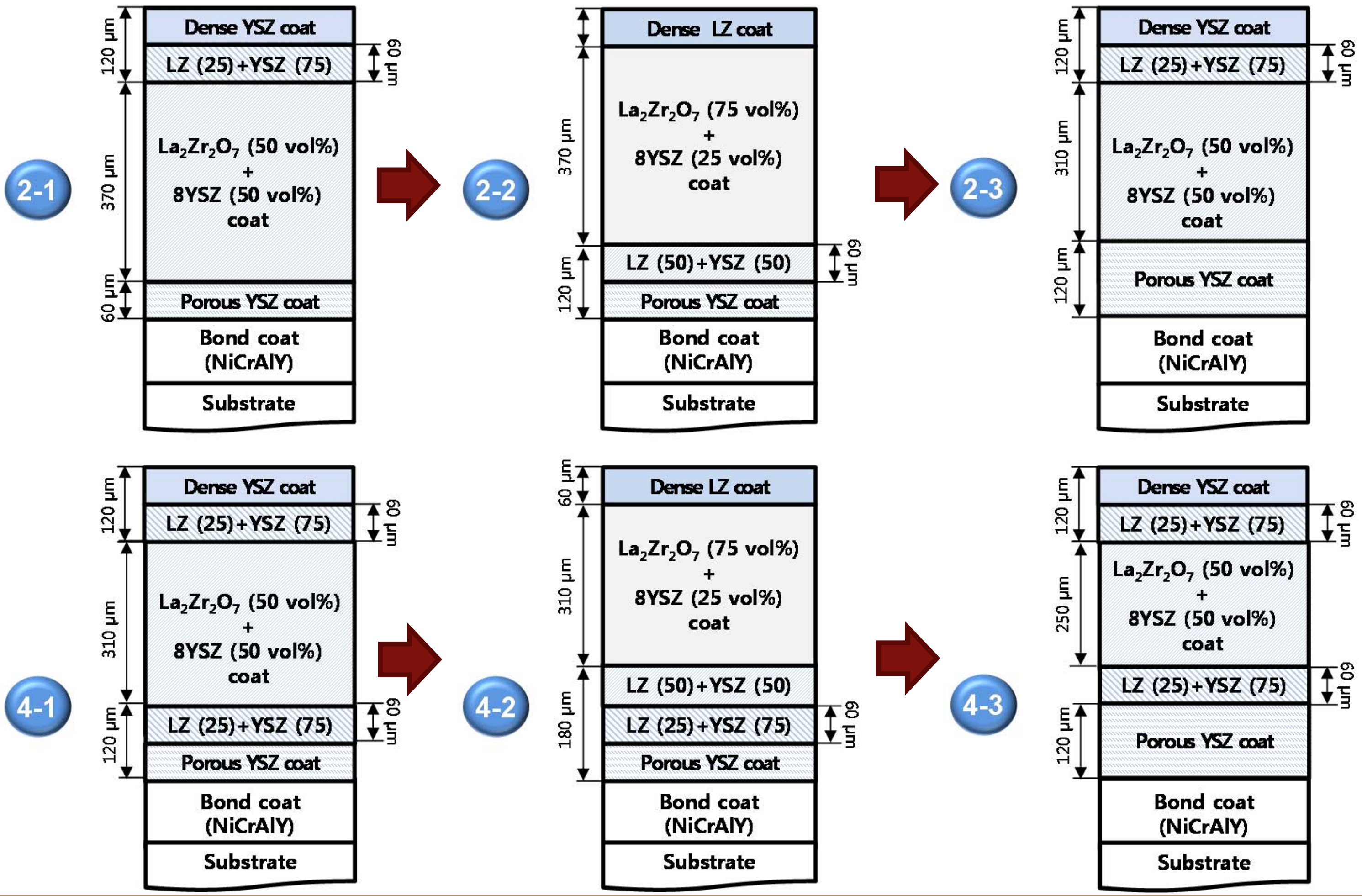
- In general, hardness increased due to densification in top coat and buffer layer, and oxidation of bond coat.

Summary

- $La_2Zr_2O_7$ powder and coating microstructure and chemistry characterizations show that $La_2Zr_2O_7$ is stable at high temperatures, which makes it suitable for TBC applications.
- Mechanical properties (hardness, bond strength) are similar to 8YSZ.
- Thermal conductivity of $La_2Zr_2O_7$ is lower than 8YSZ of similar porosity.
- Thermal properties using MD and image-based FE models calculations are in good agreement with experiments.
- Composite coatings and buffer layer are effective in improving the thermal durability of $La_2Zr_2O_7$ TBCs.
- TBC with double buffer layers showed the most outstanding thermal durability in all tests.

Future work

Thermal stability of $La_2Zr_2O_7$ coatings can be further improved by microstructure design using composite coating and buffer layers.



Publications and presentations

1. Xingye Guo, Linmin Wu, Yi Zhang, Yeongil Jung, Li Li, James Knapp, and Jing Zhang, Carbon Dioxide Adsorption on Lanthanum Zirconate Nanostructured Coating Surface: A DFT Study, *Adsorption*, 22(2), pp 159-163, 2016
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