# Thermal Barrier Coatings Hot Corrosion Studies

*Dr. Shengmin Guo*
*Drs. Yang and Khosravi of SUBR*

Louisiana State University
Department of Mechanical & Industrial Engineering
Turbine Innovation and Energy Research Center

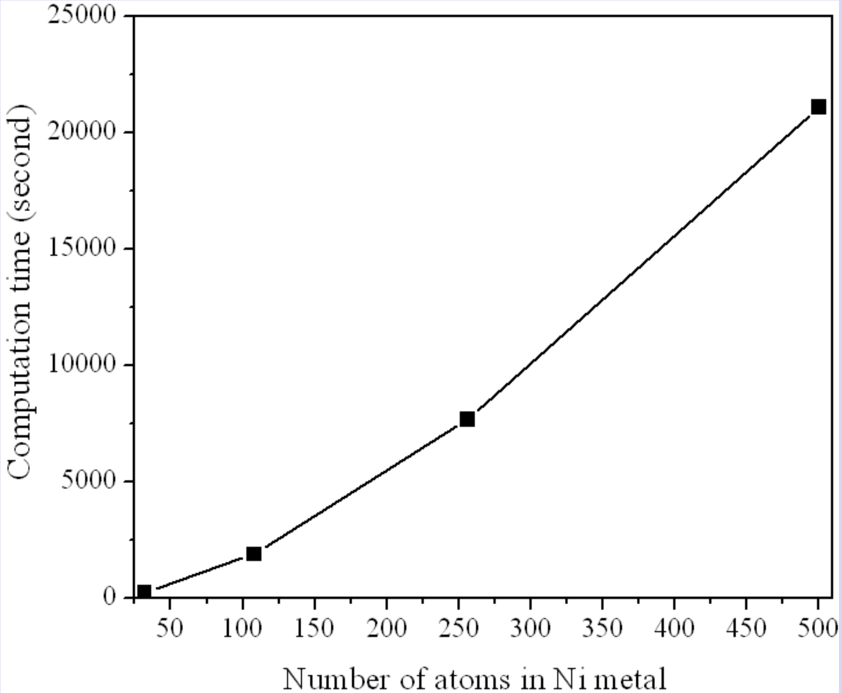
# Computational Work

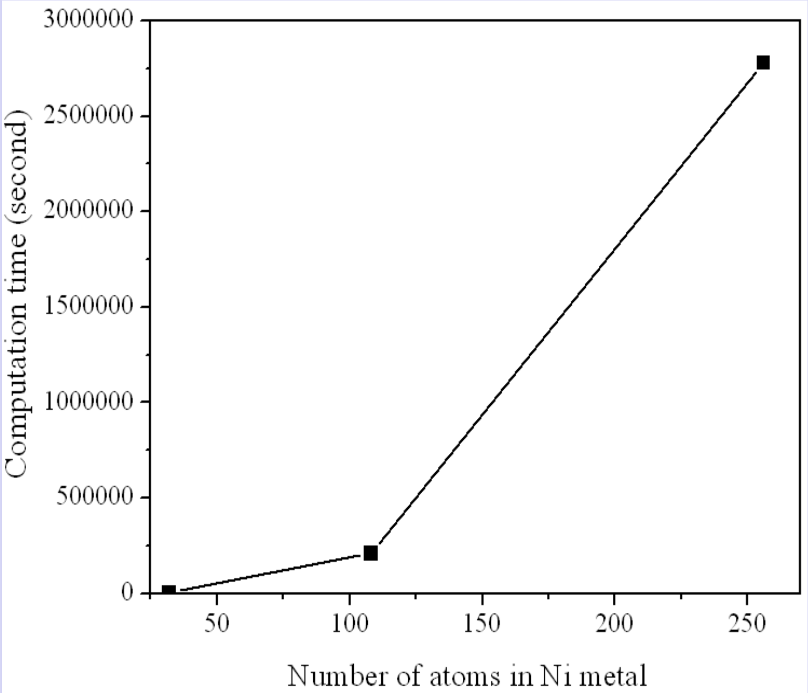
- *Ab initio* MD parallel codes;
- Potential building for top coat/bond coat;
- HPC simulations;
- Working on bond coat and top coat simulations, and data analysis;
- Validated by experiment work, the bond/top coat structure models were setup and optimized.

# Implementation and Test

- For kinetic energy fitting (KEF) based ab initio MD method we used parallelization by atom method.
- In VASP code, we used parallelization by band and plane wave methods.
- With ~300 atoms model system, VASP has optimized performance by using 128 nodes in LONI Linux cluster.

# Performance Test

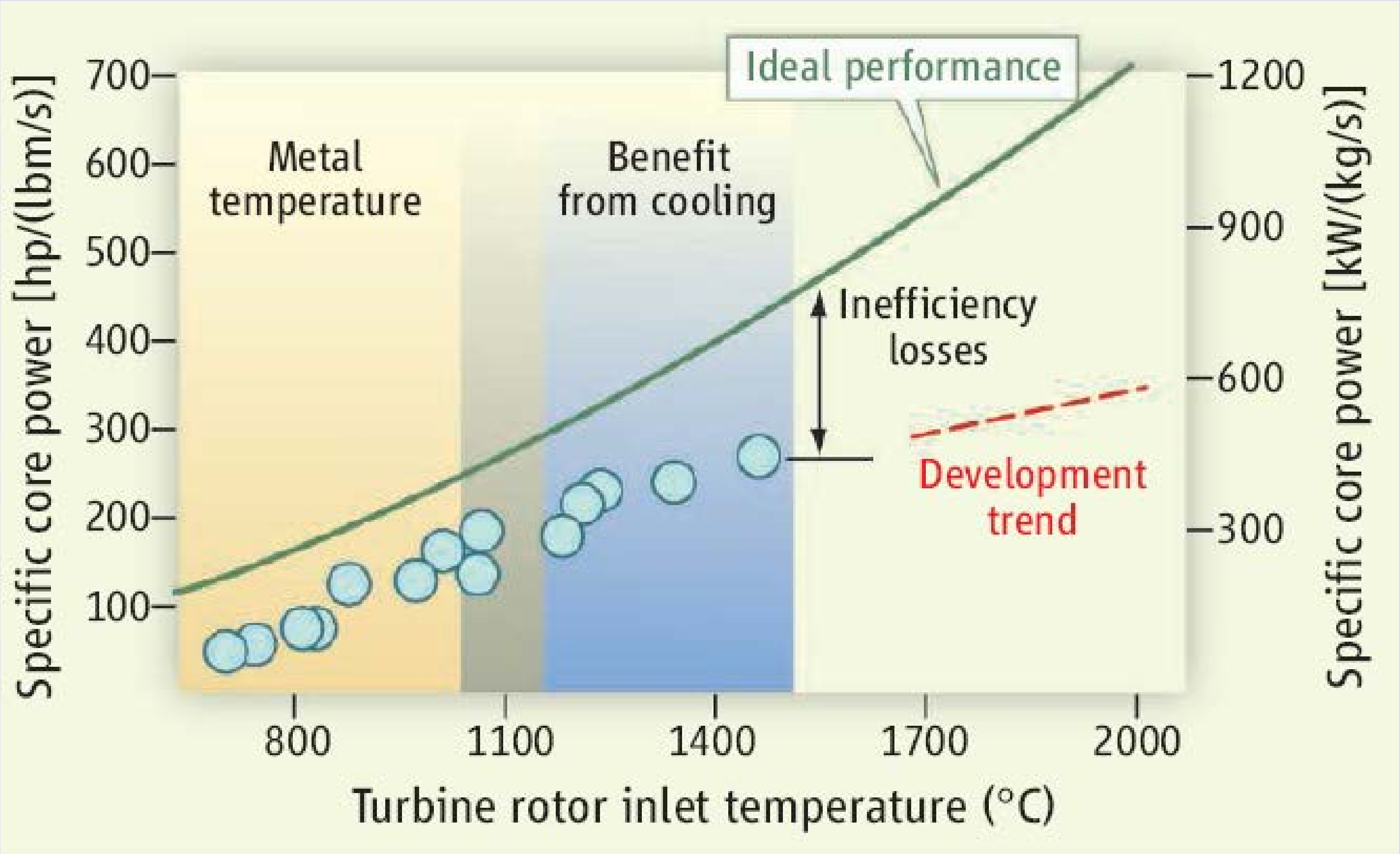


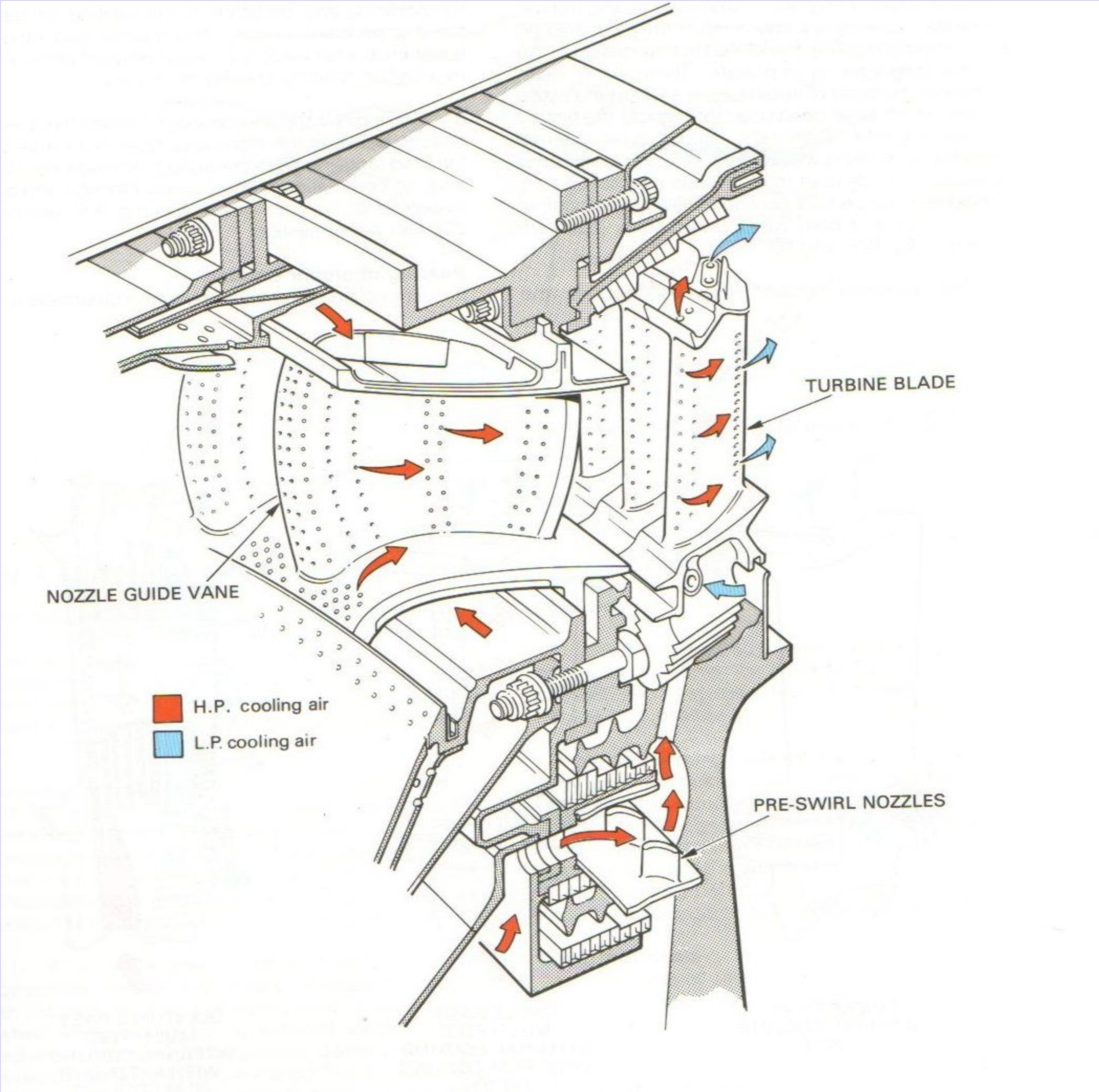

KEF MD 2000 steps with Ni run on one node.

VASP MD 2000 steps with Ni run on 32 nodes.

# The Hotter the Engine, the Better




Perepezko, 20 NOVEMBER 2009 1068 VOL 326 SCIENCE




# The Need for Turbine Cooling

Combustor Gas
1800 K

Blade Metal
1200K

Heavily cooled with air (from compressor) at 800 K

# High Temperature Coatings

- Preventing directly expose of substrate to the corrosive environment
- Providing a barrier against penetration of molten salt and gases to substrate

**High Temperature coatings**

- **Diffusional Coatings**
- **Overlay Coatings**
- **Thermal Barrier Coatings(TBCs)**

Aluminide coatings, an outer layer(CoAl or NiAl) with an enhanced oxidation resistance is developed by the reaction of Al with the Ni/Co in the base metal

**Fe,Co,Ni** ← **MCrAlY** → **Y,Zr,Mo,Hf**

- Physically bonded to substrate
- Enhancing the adhesion of TBC top coat to substrate and decreasing the oxidation and hot corrosion rate

# TBC on Nozzle Guide Vanes

# Desired Material Properties for TBC
## (Material requirements for new TBC)

- High melting point
- No phase transformation between ambient and operational temperature
- Low thermal conductivity
- Co-efficient of thermal expansion similar to the underlying alloy
- Excellent adhesion to the metallic substrate
- Low sintering rate of the porous microstructure
- Chemical inertness

# Zirconia Based TBCs

Melting point = 2690˚C

Zirconia has 3 phase transformations

**Monoclinic** ⟷ (1170ºC / 950ºC) **Tetragonal** ⟷ (2370ºC) **Cubic** ⟷ (2690ºC) **Liquid**

- Martensitic phase transformation, involves a 3-5% volume increase
- Cracking and failure in temperature cycles

Stabilizing high temperature phase of zirconia(Tetragonal)

Alloying zirconia with other oxides such as CaO,$CeO_2$, MgO, $Al_2O_3$, $Y_2O_3$

**YSZ(Yttria Stabilized Zirconia)**

**Yttria Partially Stabilized Zirconia**

# New Candidates for TBCs

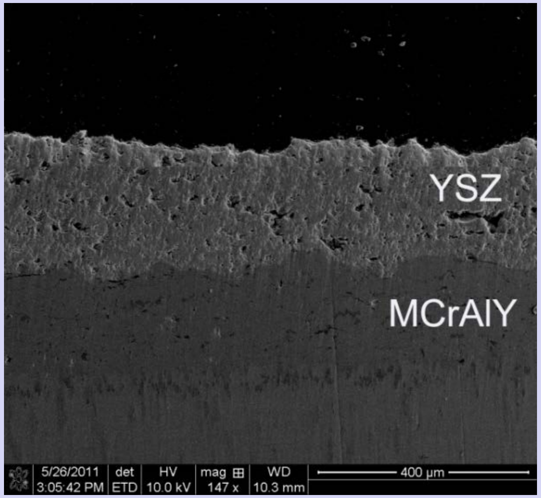
- The search for alternative coating materials other than the well established YSZ system has consisted of two main approaches:
  - alternative materials to $ZrO_2$-based systems ( Rare Earth Zirconate)
  - alternative stabilizers to $Y_2O_3$ for $ZrO_2$-based systems($CeO_2$,$Ta_2O_5$,$Nb_2O_5$, $TiO_2$)

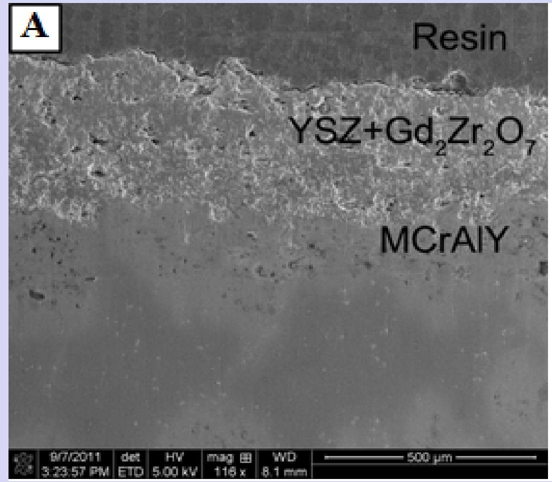
# Rare-earth Zirconate: $Gd_2Zr_2O_7$

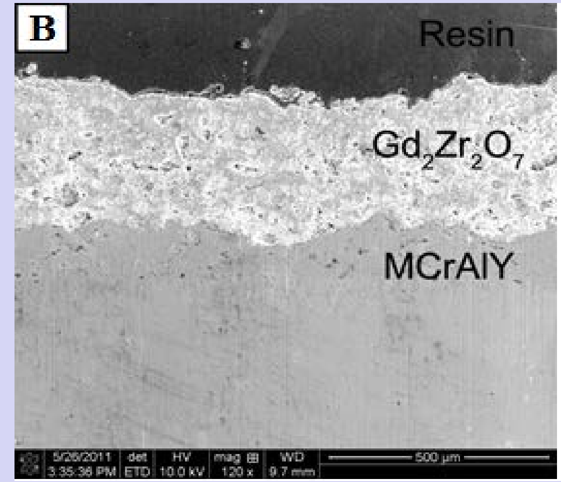
- **Alternative materials to $ZrO_2$-based systems**
  - Among high-melting ceramic materials, **Rare-earth Zirconates** ceramics are potential candidates for high-temperature thermal barrier coatings applications

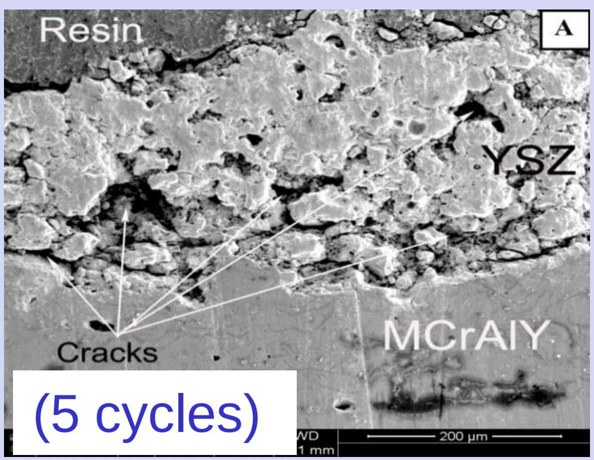
- **Gadolinium Zirconate ( $Gd_2Zr_2O_7$)**
  - $Gd_2Z_{r2}O_7$ has the lowest thermal conductivity of rare-earth zirconates
  - Relatively higher thermal expansion coefficients (CTE), higher stability, and better ability to accommodate defects than YSZ.

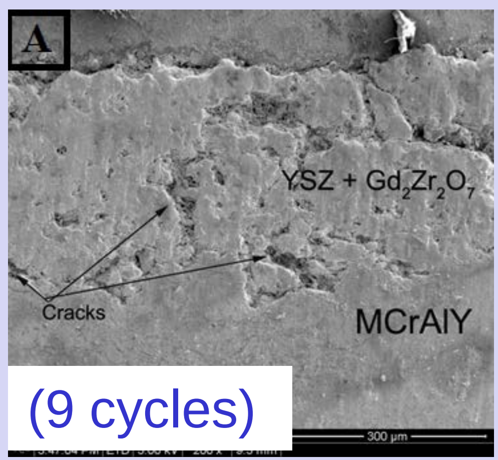
# $Gd_2Zr_2O_7$ has a better hot corrosion resistance

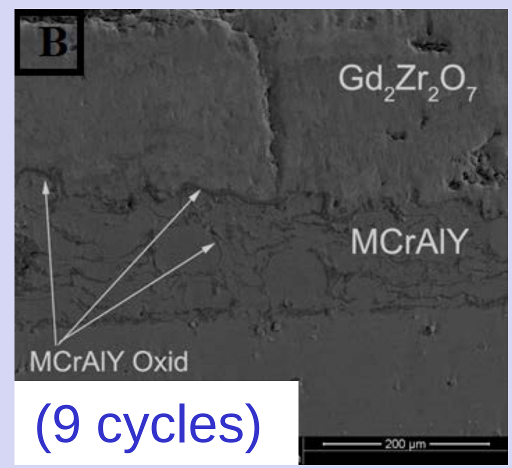


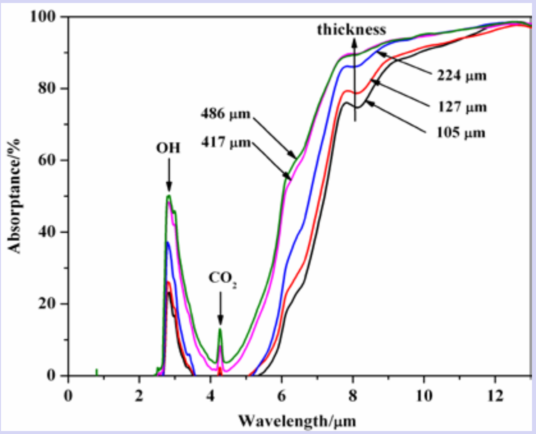



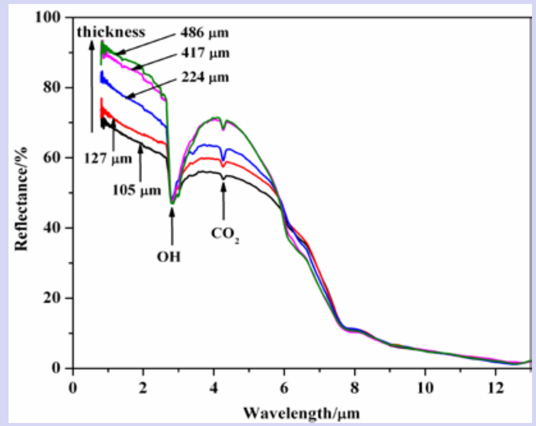



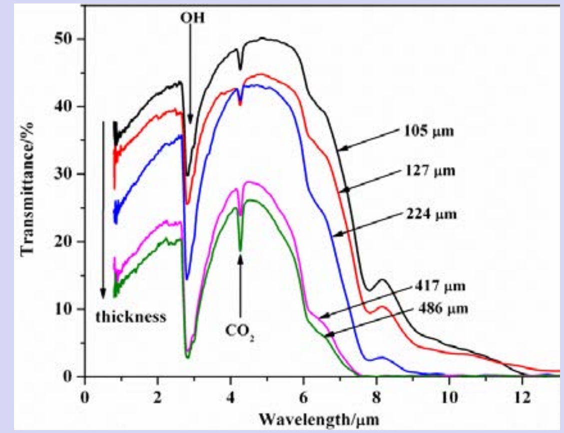




**Habibi et al. Journal of European Ceramics Society, 32 (2012) 1635–1642**

# $Gd_2Zr_2O_7$ Has Better Optical Properties




- GZ shows high Reflectance and low transmittance
- Reflect more thermal radiation energy and permit less radiation to penetrate into the BC.

Li.Wang, Jeffrey I. Eldridge, S.M. Guo, 2013, *Thermal Radiation Properties of Plasma-Sprayed $Gd_2Zr_2O_7$ Thermal Barrier Coatings*, Scripta Materialia, Volume 69, Issue 9, November 2013, Pages 674–677

# TBC Hot Corrosion Studies

## $ZrO_2$-$Y_2O_3$-$Ta_2O_5$ Systems

# High Temperature Corrosion

- **Type one ( 850-1100˚C)**

  Vanadium and Sulfur in low quality fuels

  ( Sodium sulfate and vanadium oxide)

- **Type two ( 600-800˚C)**

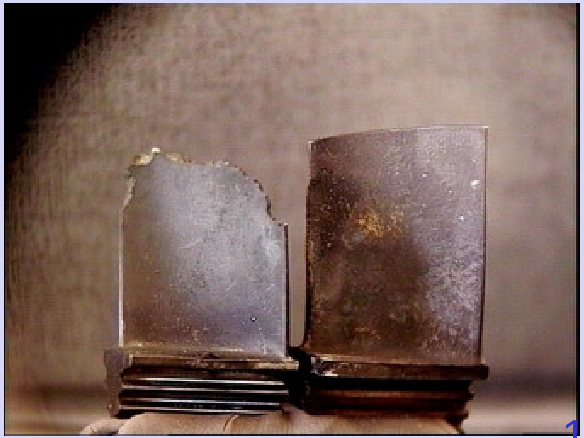
  Pitting, forming metal sulfates

Sodium sulfate - Cobalt sulfate,

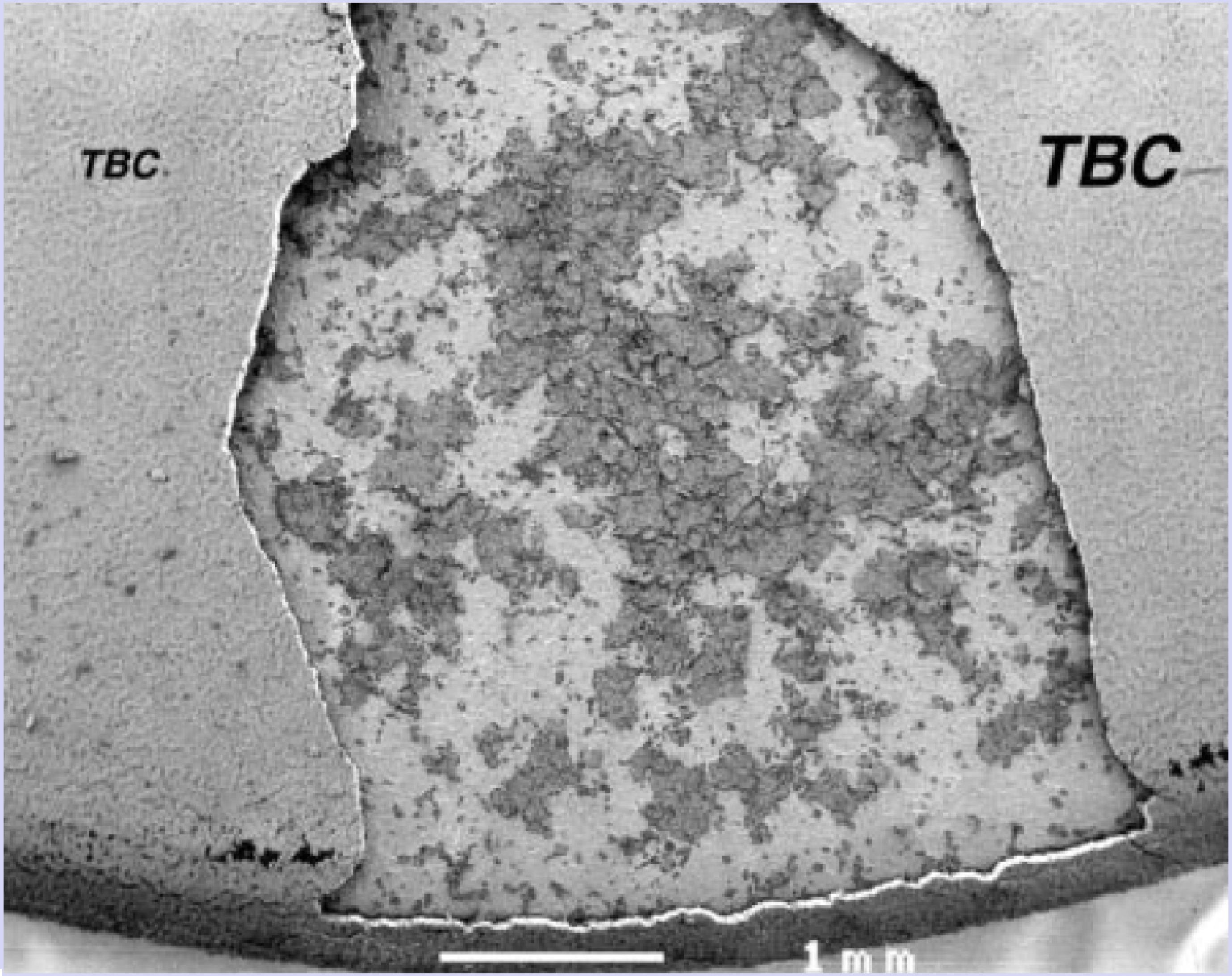
Sodium sulfate - Nickel sulfate

• Hot corrosion mechanism

- For alloys: breaking the protective oxide scale and penetration of molten salt in substrate
- For **coatings:** reacting with bulk of coating, inducing stress and phase transformation in coating which leads to **crack formation** and **spallation**



# Failure of TBCs



# Experimental Studies

Substrate Selection

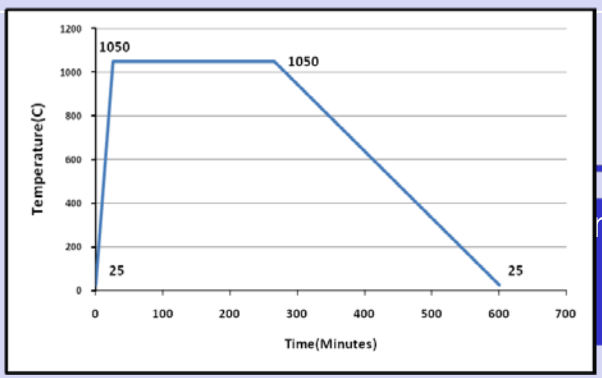
Coatings

- MCrAlY
- TBC
  - YSZ
  - $Gd_2Zr_2O_7$
  - $ZrO_2+Ta_2O_5$
  - $YSZ+Ta_2O_5$

**Vanadium Oxide**
**Sodium Sulfate**
**CMAS**

700 -1400 °C

Hot Corrosion




Analysis

nt
is

**Microstructure Analysis (SEM)**

- Surface
- Cross-section

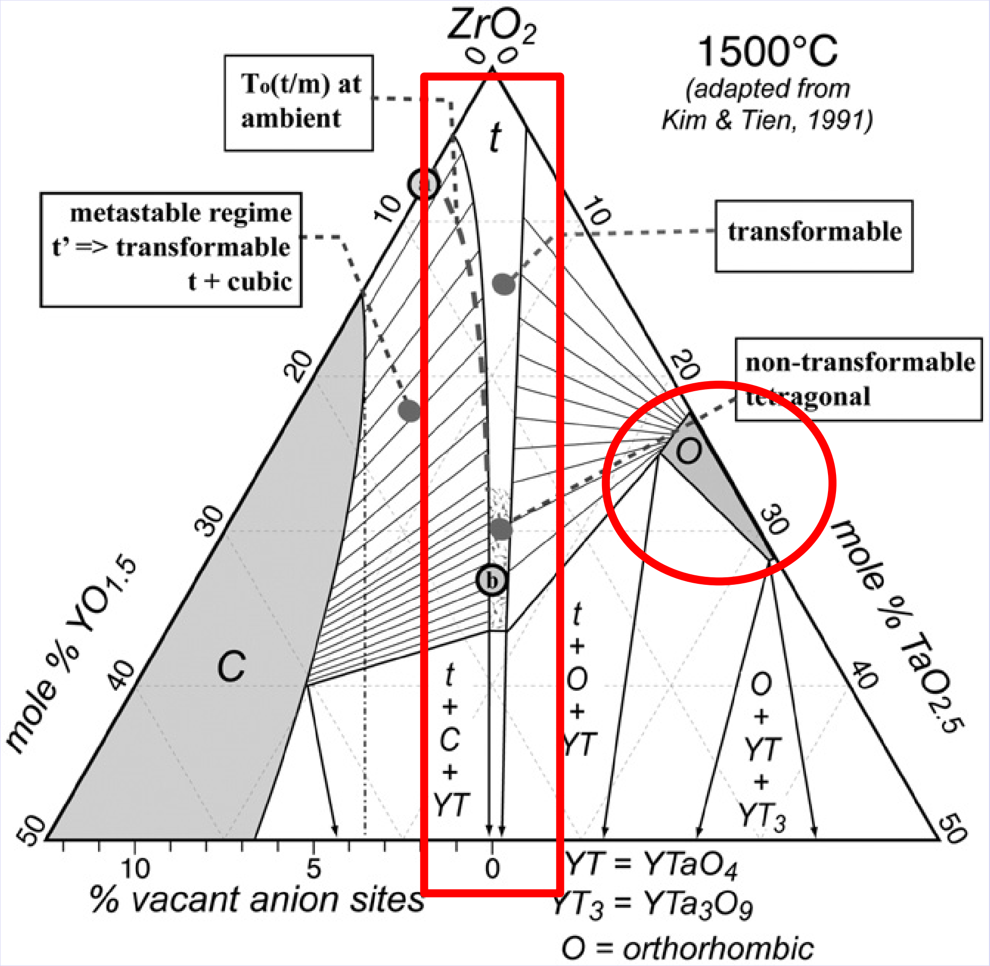
**CTE, Thermal Conductivity**

# Why Tantalum Oxide ?

- $Ta_2O_5$ is a pentavalent oxides and it has a melting point over 1800˚C.
- On heating it undergoes a phase transformation at 1460˚C which is well above the typical turbine surface temperatures.
- Substituting Y with Ta should lower the activity and diffusivity of Y in zirconia solid solution thus make this composition more resistant to hot corrosion(defect association, Mayo 2002)

# The Amount of Tantalum Oxide ?

- **Previous reports on $Y_2O_3$-$Ta_2O_5$ co-doped zirconia systems mainly have a focus on the system stability with equal Y and Ta.**
- **The investigated compositions generally have a low $Ta_2O_5$ content of less than 20 wt%.**
- Our Focus: Zirconium tantalum oxides with single Orthorhombic phase ($TaZr_{2.75}O_8$)



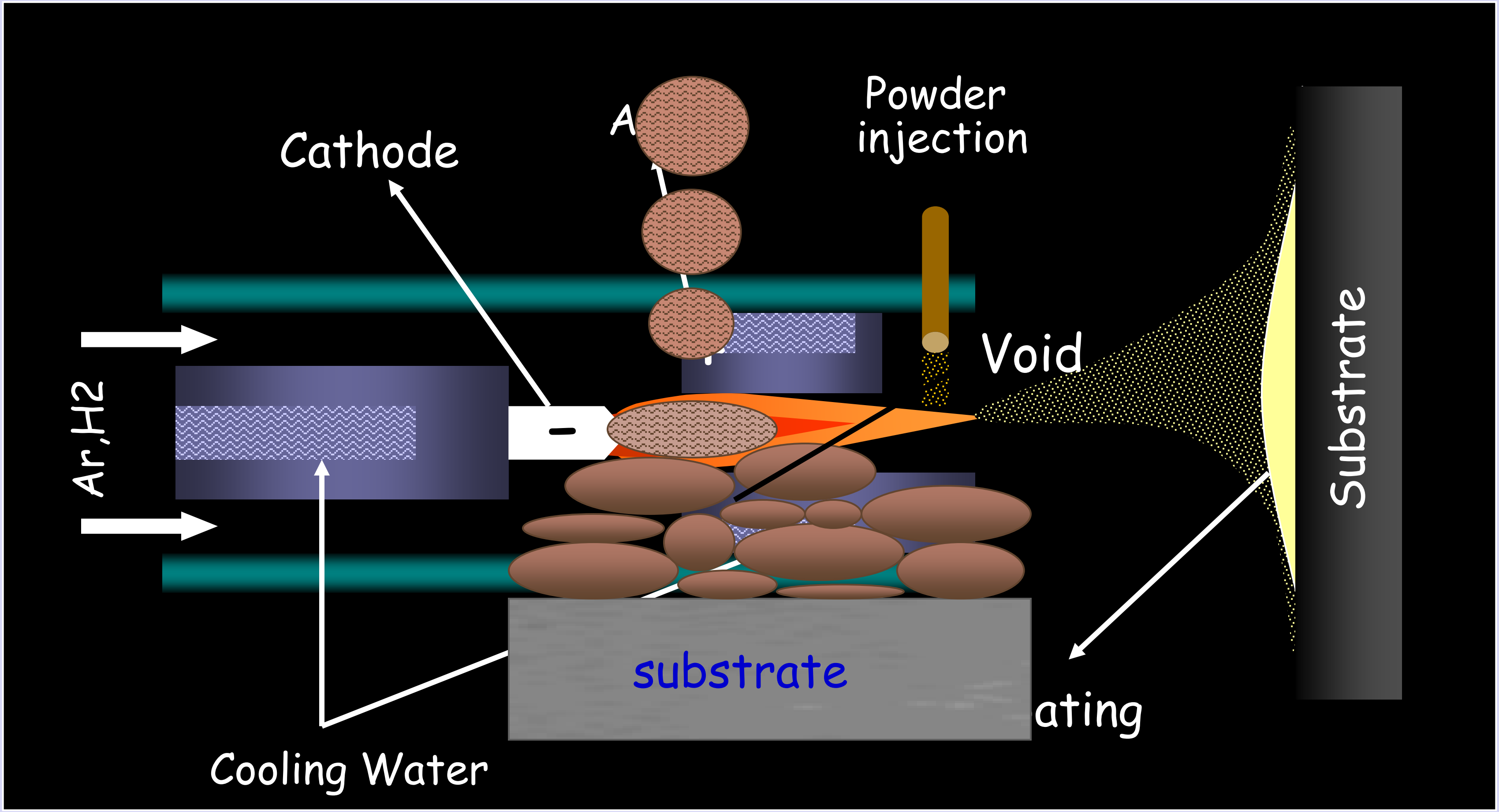

Pitek and Levi, Surf. Coat. Technol. 201 (2007) 6044–6050

# Deposition Methods

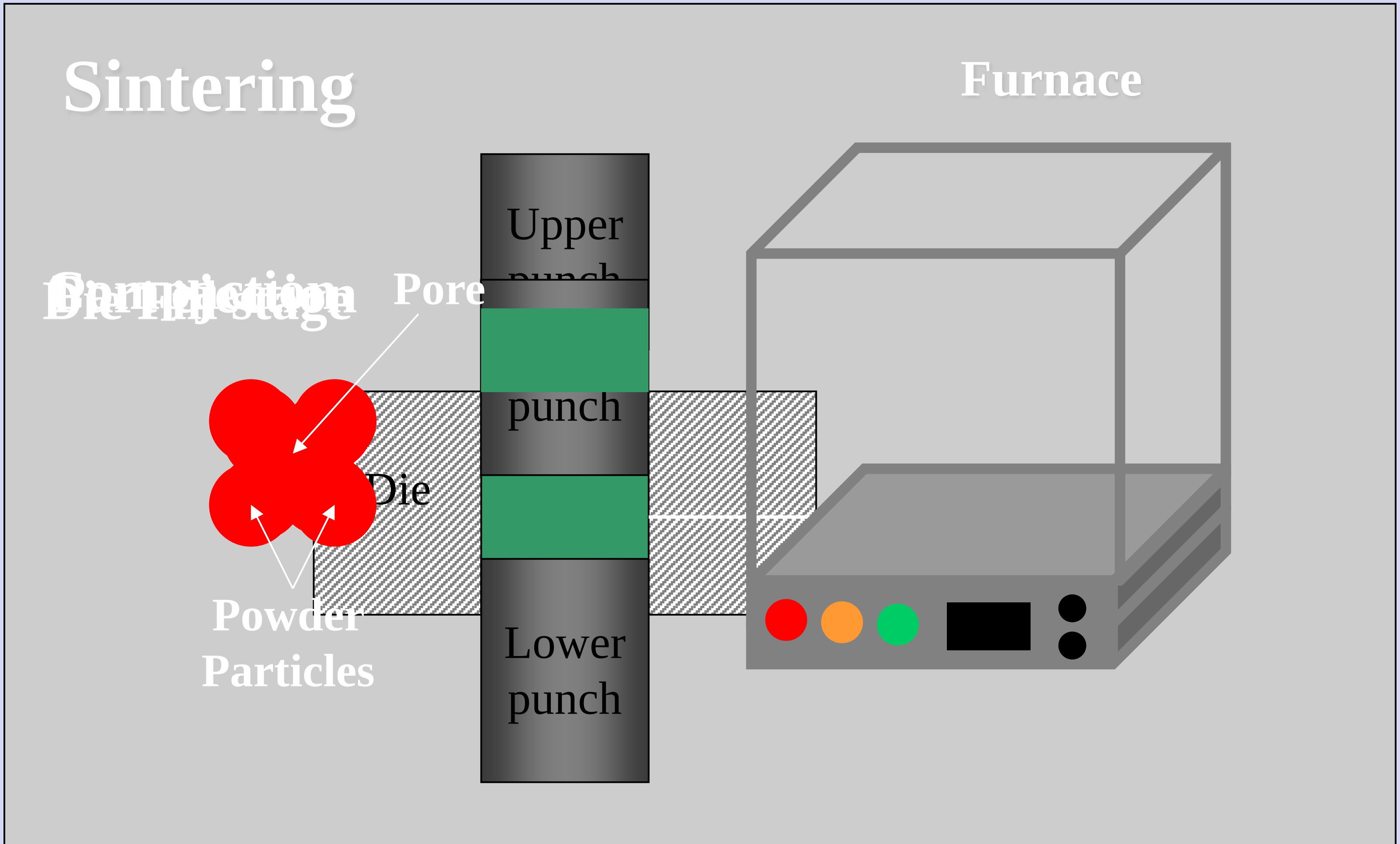
- **Mainly 3 methods ( depends on coating material, substrate shape, availability of powders and cost)**
  - ***Air Plasma Spray (APS)***
  - ***Electron Beam physical vapor deposition (EB-PVD)***
  - ***High Velocity Oxyfuel (HVOF)***

  - ***Conventional pressing and sintering (Powder metallurgy)***

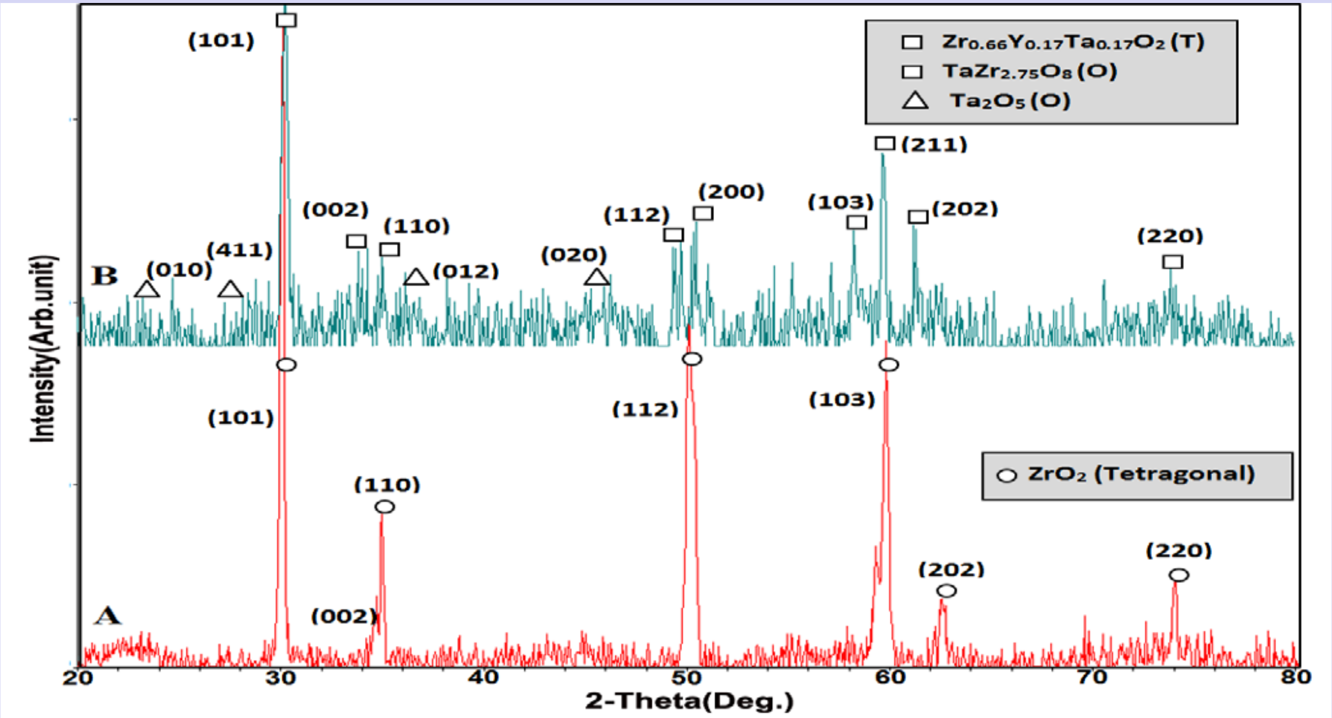
# AIR PLASMA SPRAY(APS)



# Pressing and Sintering

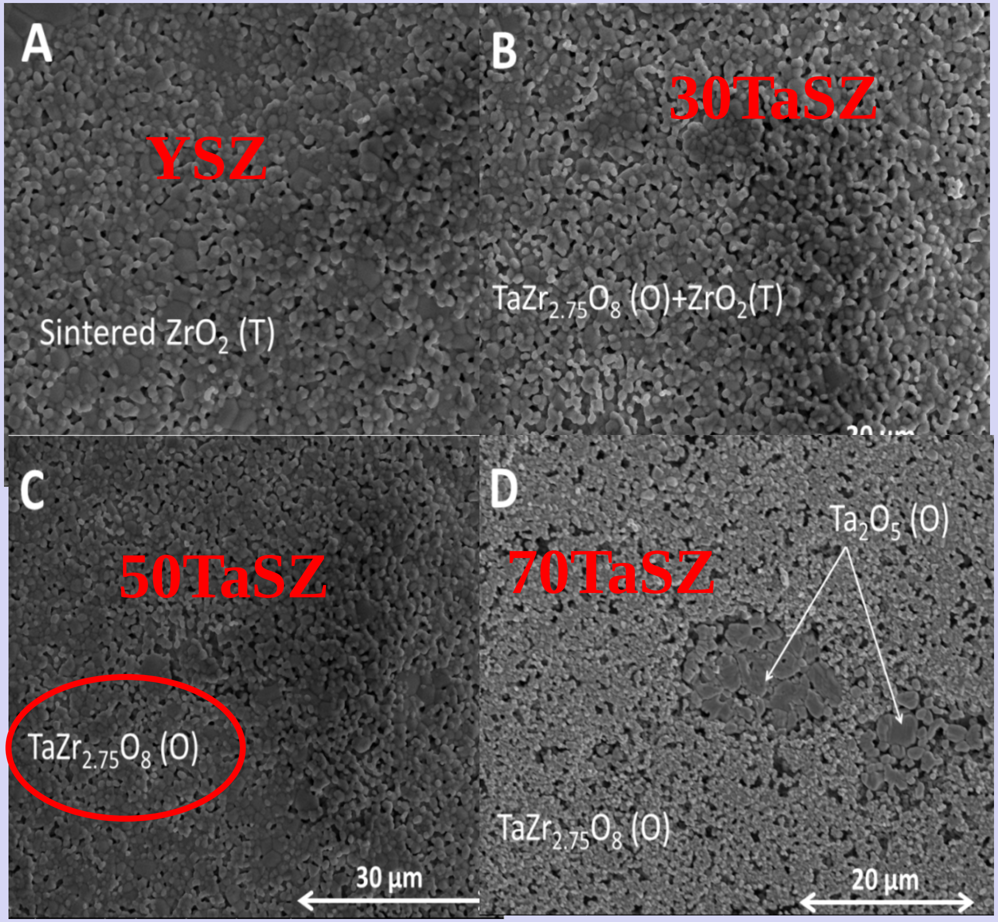


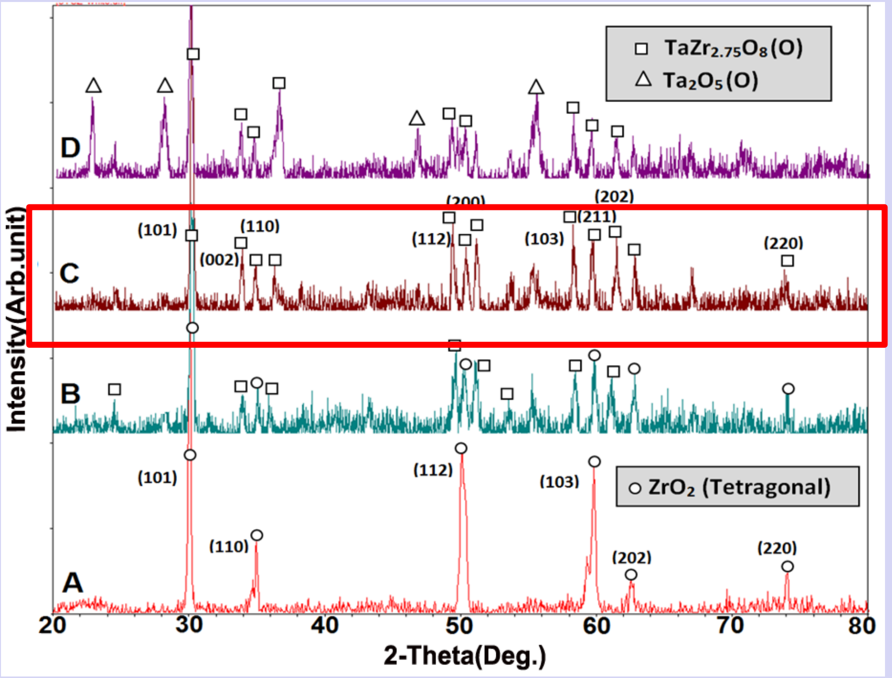
# As-Received Samples




- YSZ is tetragonal zirconia.
- 50TaYSZ sample (50wt%YSZ+50wt%$Ta_2O_5$) forms complex Zirconium tantalum (Yttrium) oxide ($TaZr_{2.75}O_8$ and $Zr_{0.66}Y_{0.17}Ta_{0.17}O_2$)
- Orthorhombic phase zirconium tantalum oxide : $TaZr_{2.75}O_8$

# As-Received Samples

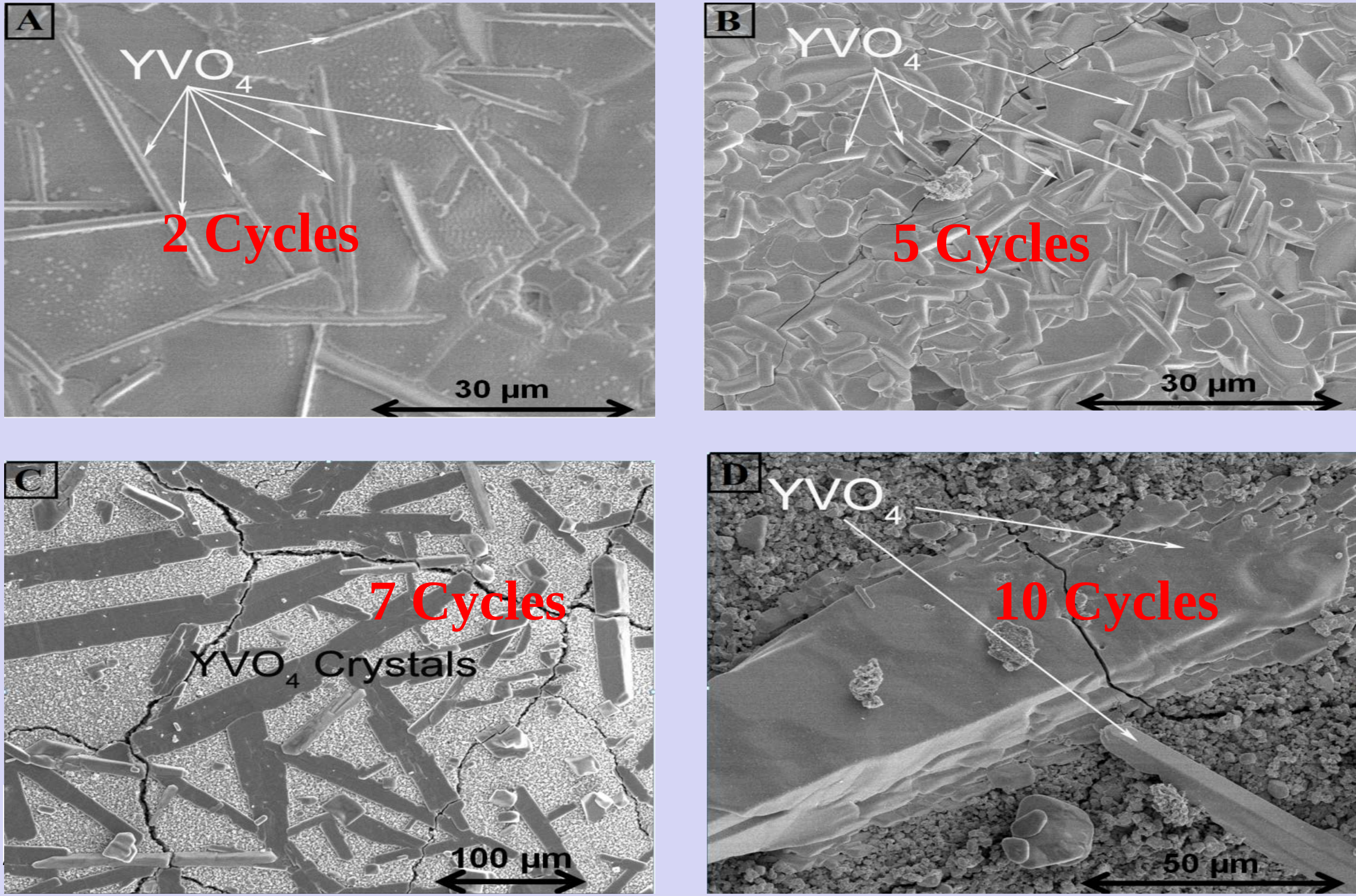


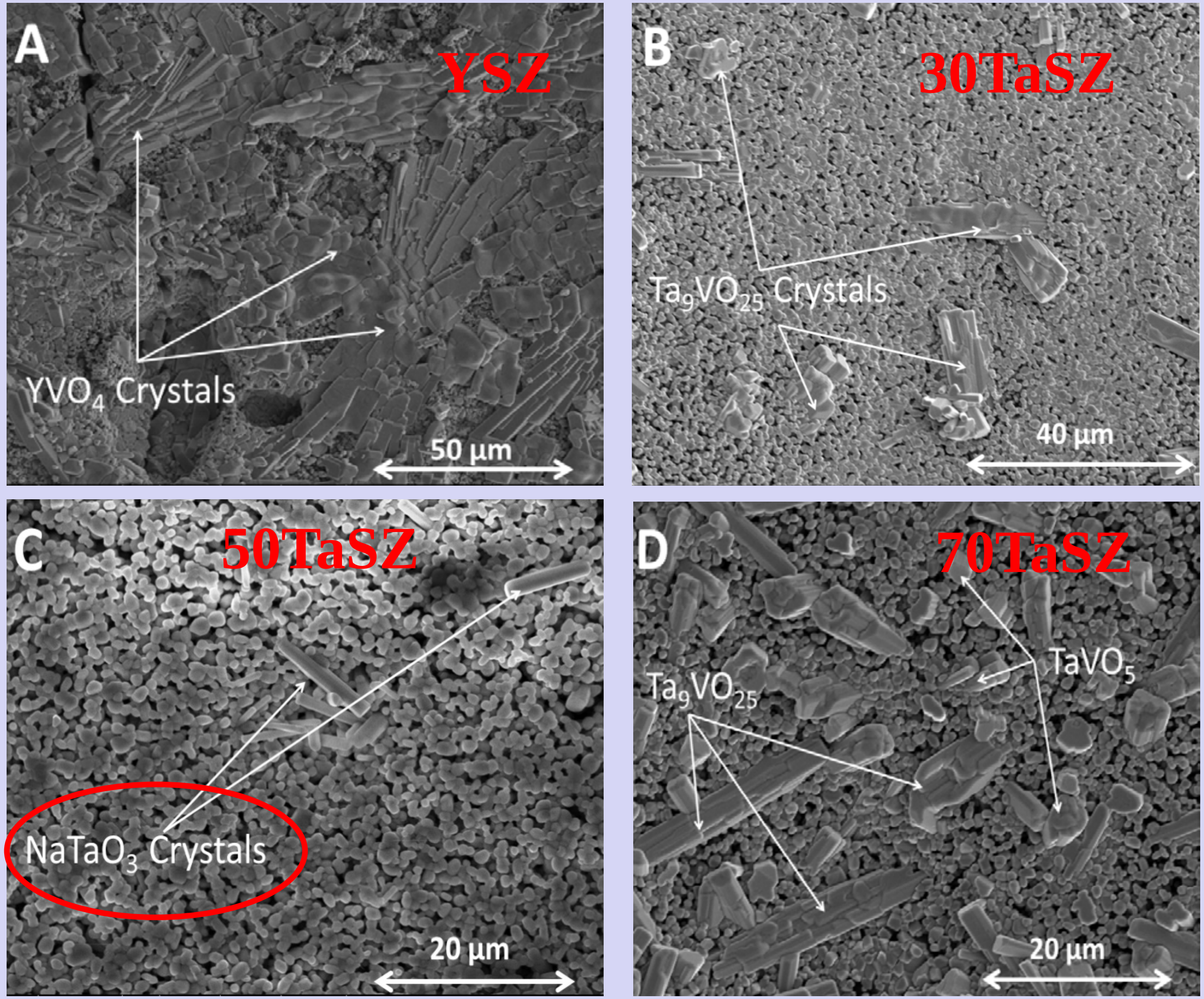

**SEM Surface image and XRD patterns of as-received A) YSZ, B) 30TaSZ, C) 50TaSZ and D) 70TaSZ**

**Orthorhombic phase zirconium tantalum oxide : $TaZr_{2.75}O_8$**

# YSZ Hot Corrosion Results: Yttrium Vanadate



# Hot Corrosion Results




SEM surface images of samples after hot corrosion in Sodium Sulfate + Vanadium Oxide at 1100˚C for **40 hours**.

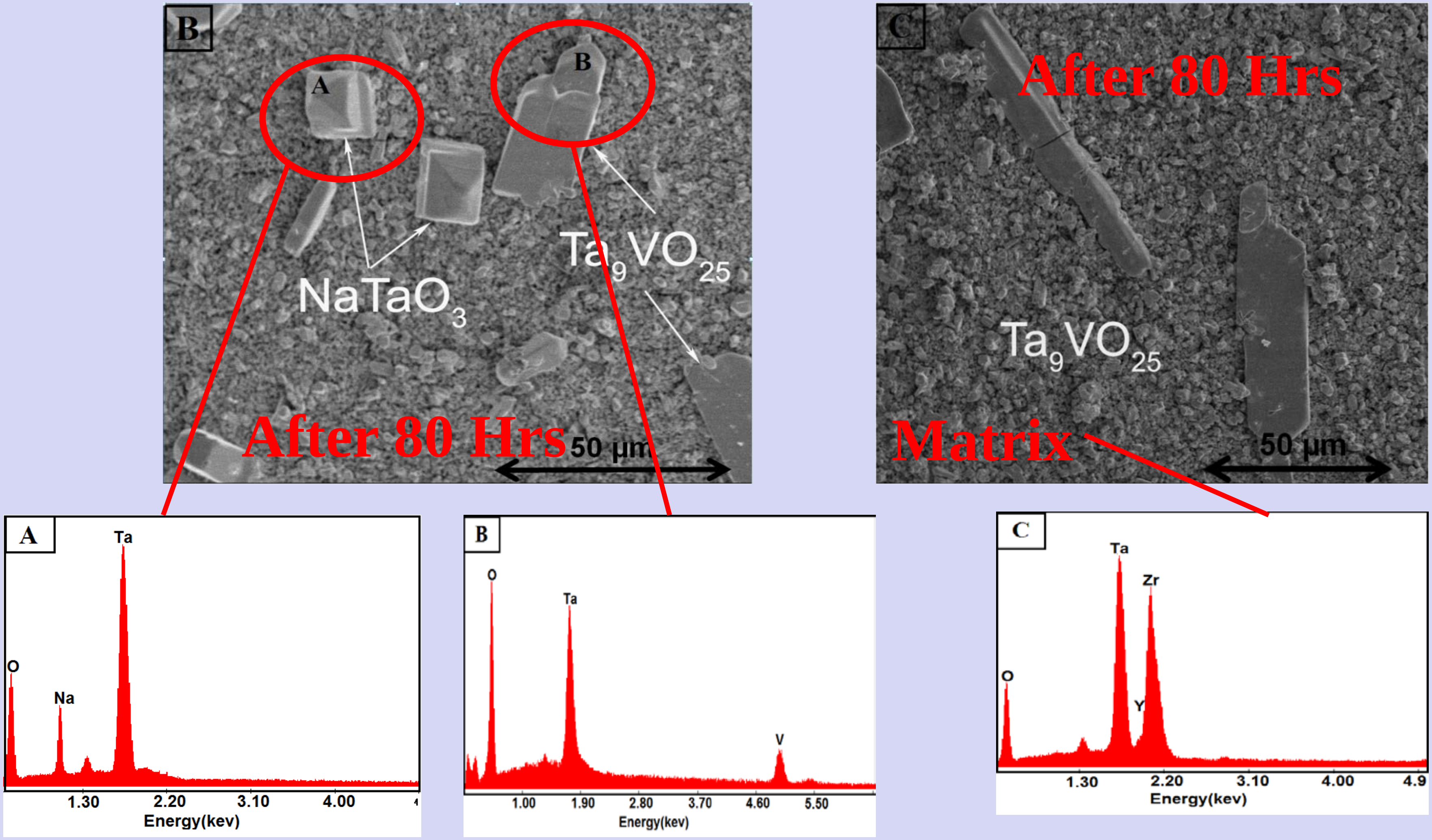
A) YSZ,

B) 30TaSZ

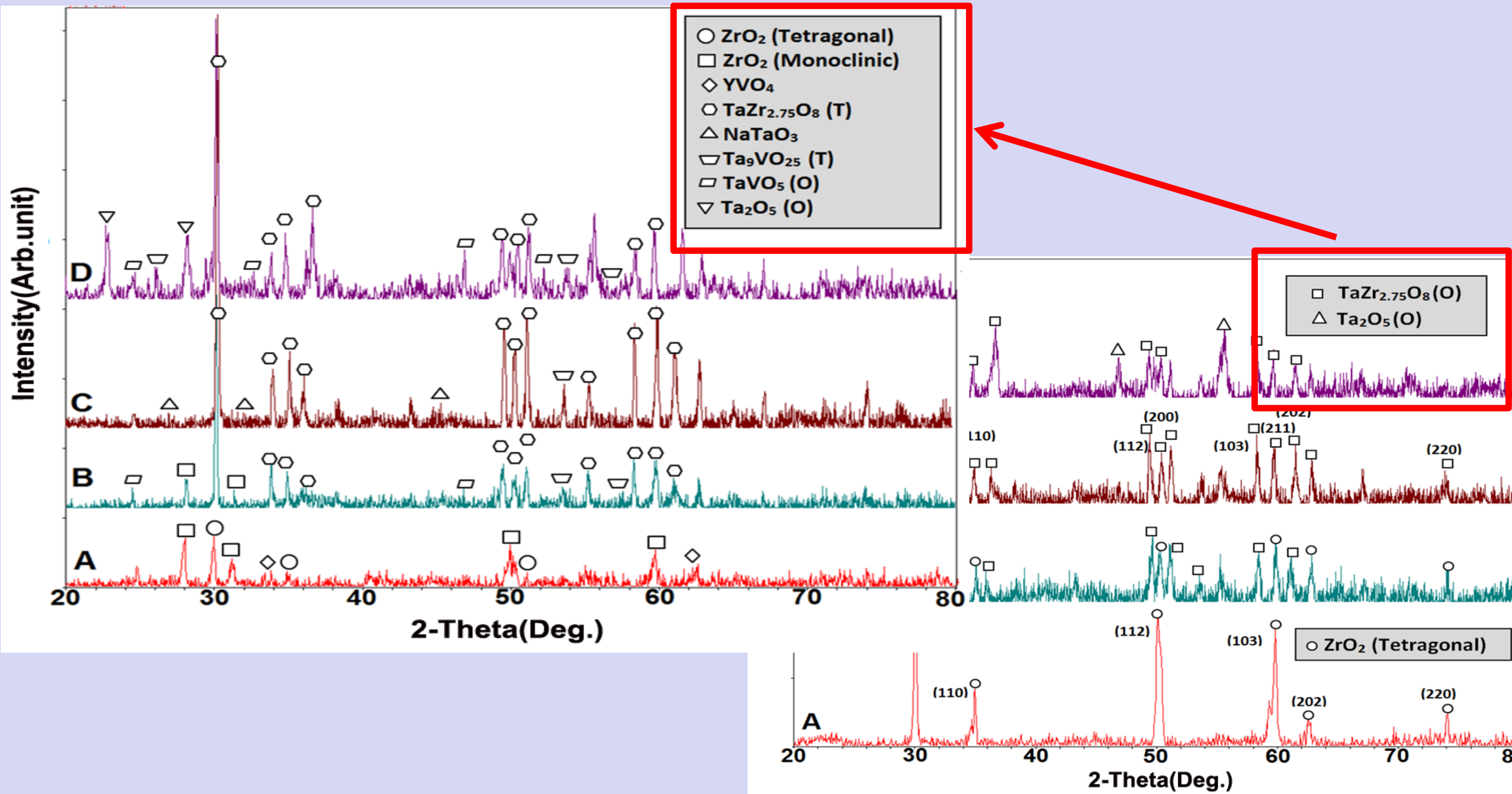
C) 50TaSZ

D) 70TaSZ

# 50TaYSZ Hot Corrosion Results



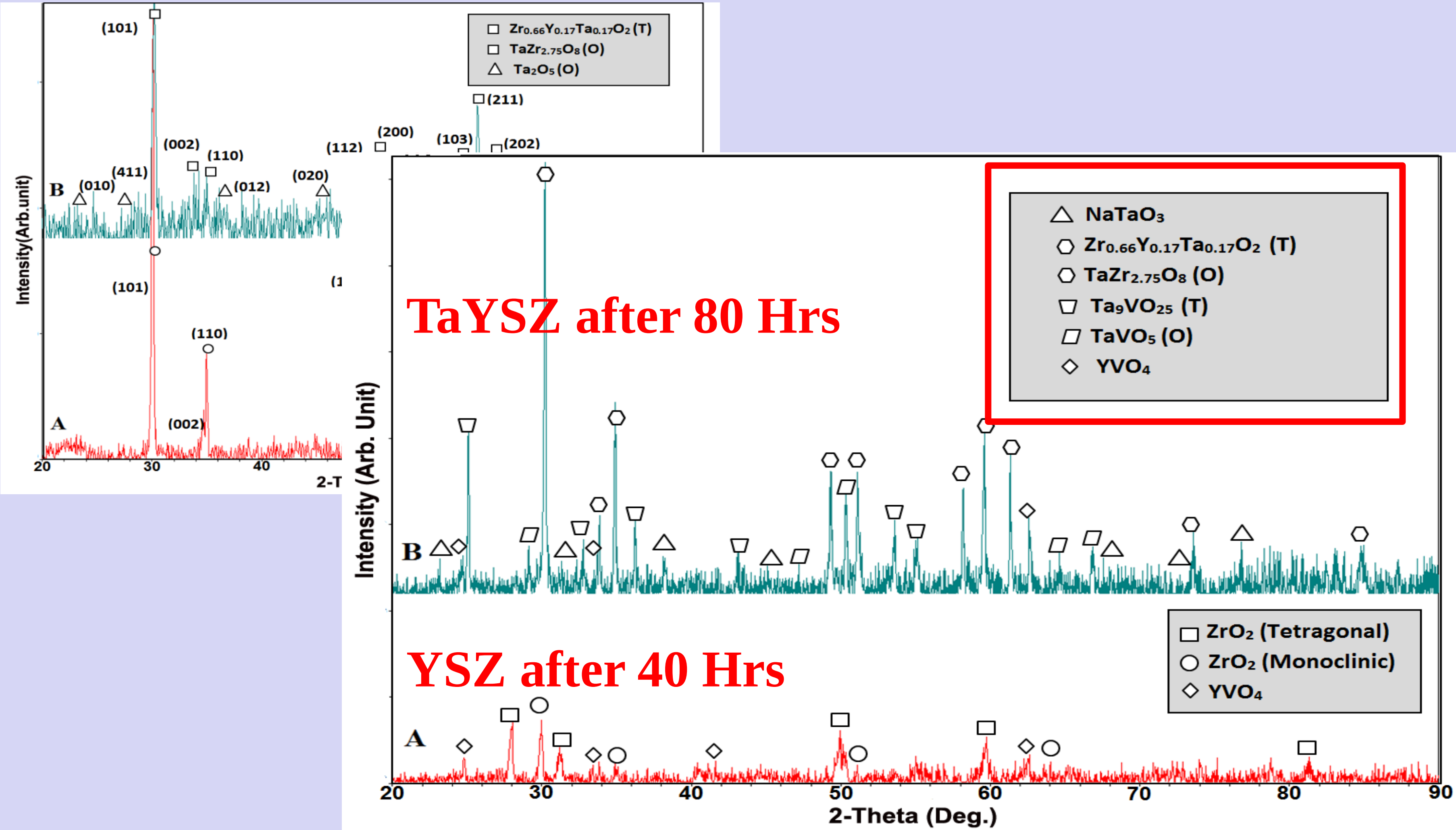
# TaSZ Hot Corrosion Results




**XRD patterns of A) YSZ, B) 30TaSZ, C) 50TaSZ and D) 70TaSZ after Hot corrosion for 40 Hrs**

LSU

# TaYSZ Hot Corrosion Results



# Hot Corrosion Reactions

- Sodium Metavanadate ($NaVO_3$) forms due to the presence of both Vanadium Oxide and Sodium Sulfate :

$$V_2O_5 + Na_2SO_4 \rightarrow 2(NaVO_3) + SO_3$$

  – For 30TaSZ, 50TaSZ and 70TaSZ, the possible reactions that would have produced those identified reaction products include:

$$TaSZ\ (Ta_2O_5)\ (s) + NaVO_3\ (l) \rightarrow NaTaO_3(s) + TaVO_5(s)$$

$$TaSZ\ (5Ta_2O_5)\ (s) + NaVO_3\ (l) \rightarrow NaTaO_3(s) + Ta_9VO_{25}(s)$$

- $V_2O_5$ may also react with $Ta_2O_5$ directly at elevated temperature. According to $Ta_2O_5$-$V_2O_5$ phase diagram, in temperatures lower than 1200˚C, two possible components are $TaVO_5$ and $Ta_9VO_{25}$

$$V_2O_5\ (l) + TaSZ\ (Ta_2O_5)\ (s) \rightarrow 2TaVO_5\ (s)$$

$$V_2O_5\ (l) + 9\ TaSZ\ (Ta_2O_5)\ (s) \rightarrow 2Ta_9VO_{25}\ (s)$$

LSU

# 50TaYSZ Hot Corrosion Reactions

**$ZrO_2\ (Y_2O_3) + 2(NaVO_3) \rightarrow ZrO_2 + 2(YVO_4) + Na_2O$ (1)**

**$TaYSZ\ (Ta_2O_5)\ (s) + NaVO_3\ (l) \rightarrow NaTaO_3(s) + TaVO_5(s)$ (2)**

**$TaYSZ\ (5Ta_2O_5)\ (s) + NaVO_3\ (l) \rightarrow NaTaO_3(s) + Ta_9VO_{25}(s)$ (3)**

- After 80 hours, only very weak $NaTaO_3$, $TaV_9O_{25}$ , $TaVO_5$ and $YVO_4$ XRD peaks could be detected on the surface of the TaYSZ sample.

- Vast areas of **$Zr_{0.66}Y_{0.17}Ta_{0.17}O_2$** and **$TaZr_{2.75}O_8$** were identified intact after Hot corrosion, it is more likely that the excess $Ta_2O_5$ in the sample reacted with the molten salt to form the above mentioned products.

- No spallation of the sample was found even after 80 hours (twenty 4-h cycles) of testing at 1100˚C, which is twice the YSZ test duration.

LSU

# Computational Work

- Gibbs Free Energy of Formation data

There is no data in literature for Gibbs Free energy of Formation of $TaVO_5$, $Ta_9VO_{25}$ and $NaTaO_3$, So *ab initio* density functional theory (DFT) based electronic structure simulations to obtain the relevant thermodynamic data

**$ZrO_2$ ($Y_2O_3$) + 2($NaVO_3$) → $ZrO_2$ + 2($YVO_4$) + $Na_2O$ (1)**

**Ta(Y)SZ ($Ta_2O_5$) (s) + $NaVO_3$ (l) → $NaTaO_3$(s) + $TaVO_5$(s) (2)**

**Ta(Y)SZ (5$Ta_2O_5$) (s) + $NaVO_3$ (l) → $NaTaO_3$(s) + $Ta_9VO_{25}$(s) (3)**

| Substance | $Y_2O_3$ | $NaVO_3$ | $YVO_4$ | $Na_2O$ | $Ta_2O_5$ | $NaTaO_3$ | $TaVO_5$ | $Ta_9VO_{25}$ |
|---|---|---|---|---|---|---|---|---|
| Gibbs E (kJ/mol) | -2713.24 | -1501.93 | -3960.34 | -494.51 | -1719.71 | -1304.14 | -2048.53 | -10693.86 |

- $YVO_4$ (Eq.1) is much more stable than both $NaTaO_3$ and $TaVO_5$ (Eqs.2 and 3)
- Thermodynamic Data confirms experimentally observed faster reaction of Eq.1 than Eqs. 2 and 3.

# Conclusions

- **Morphologies**
  - At the beginning of the hot corrosion process, the hot corrosion products ($TaVO_5$, $Ta_9VO_{25}$ and $YVO_4$) have dendritic like shapes; then as the hot corrosion proceeds, these hot corrosion products become larger and their morphologies change to rod/plate-like shapes.
- **YSZ sample**
  - Production of $YVO_4$, leaching $Y_2O_3$ from the YSZ , progressive tetragonal to monoclinic destabilization transformation, crack formation
- **$ZrO_2$-$Ta_2O_5$ and $ZrO_2$-$Y_2O_3$**
  - Based on thermodynamic data and basicity of $Y_2O_3$ and $Ta_2O_5$ and their tendency to react with molten salt, the growth rates of $NaTaO_3$ and $TaVO_5$ are slower than that of $YVO_4$ in the prolonged hot corrosion tests which indicate better stability of zirconia, stabilized with $Ta_2O_5$ rather than with $Y_2O_3$.
- **$ZrO_2$ - 50 wt.% $Ta_2O_5$**
  - hot corrosion resistance of 50TaSZ is the best. This sample has a near single orthorhombic phase of $TaZr_{2.75}O_8$, which is highly stable in high temperatures and resistant to hot corrosion attack in molten salts.

Dr.Guo's Group

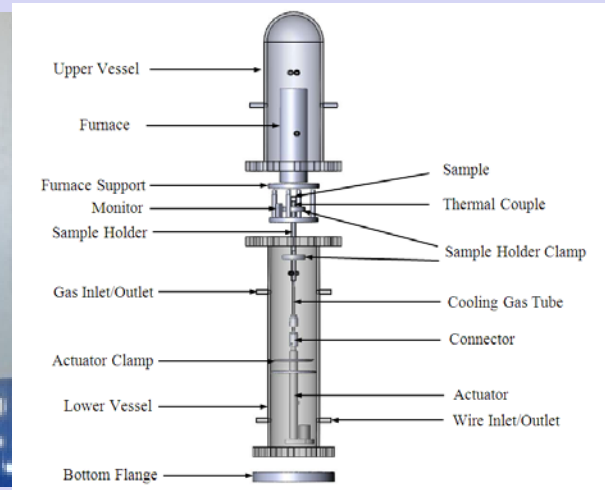
**Funded by NASA, DOE, BOR, etc.**

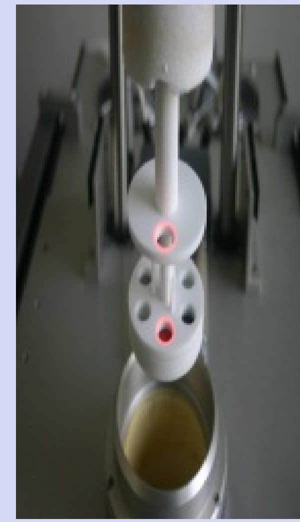
# Studies on TBCs


# Dr.Guo’s Group

**Funded by NASA, DOE, BOR, etc.**

# Coating Characterizations



Thank you for

your attention!