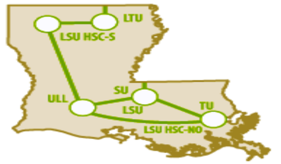


Computational Design and Experimental Validation of New Thermal Barrier Systems

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

Southern University
LONI Institute

Drs. Shengmin Guo, Shizhong Yang, and Ebrahim Khosravi

Outline

- Project Objectives
- Introduction
- Approach
- Results
- Conclusions and Future Work
- Acknowledgement

Project Objectives

- To develop a novel TBC design/simulation method, based on the integration of *ab initio* density functional theory (DFT) method with classical molecular dynamics (MD) method.
- To perform high performance computer (HPC) simulation.
- To perform experimental validation.

FY 2012 Objectives

- Cr-Y/Ta bond-coat potential building and computer simulation.
- Ta:YSZ top-coat potential building and computer simulation.
- Bond coat and top coat sample preparation.

Introduction

- Sustain a high working temperature (> 1200 °C)
- Better oxidation and molten deposit corrosion resistance.
- Our approach:
  - A Ta/Cr doped system
  - Theoretical design and simulation (HPC computational screening & optimization)
- Perform experimental validation.

Approach

- *Ab initio* DFT method is accurate for material design but the cell size is limited to a few hundreds ~ a thousand or so atoms.
- Classical MD method is efficient but the accuracy of the method depends on the potential used.
- Our method will integrate the above two advantages together into TBC MD simulation.

Approach

- *Ab initio interatomic* potential generating. The Hamiltonian:

$$\mathrm{E}_{\mathrm{total}}(\rho)=\mathrm{T}+\sum_{lm}\int\rho(\vec{r})dv\frac{-e^{2}Z_{m}}{\left|\vec{r}-\vec{\tau}_{m}-\vec{R}_{l}\right|}+\frac{1}{2}\int\frac{\rho(\vec{r})\rho(\vec{r}\,')}{\left|\vec{r}-\vec{r}\,'\right|}dv\,dv'+\mathrm{E}_{\mathrm{xc}}(\rho)+\frac{1}{2}\sum_{mn}\frac{e^{2}Z_{m}Z_{n}}{\left|\vec{\tau}_{m}-\vec{\tau}_{n}\right|}$$

The kinetic energy term T is expressed as an UBER relation:

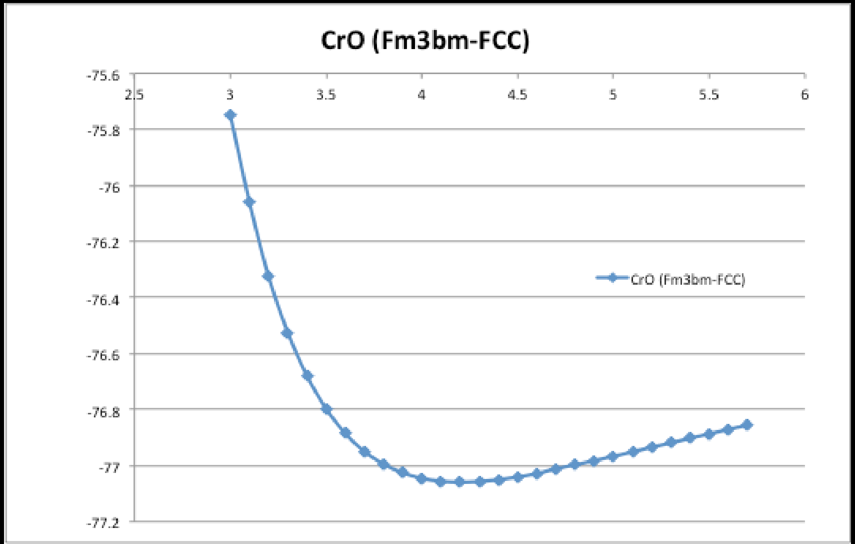
$$\mathrm{T}\equiv\mathrm{E}_{\mathrm{rep}}=\frac{1}{2}\sum_{\substack{i,j\\(i\neq j)}}\varepsilon d_{ij}^{\,n}\exp\left(-\frac{d_{ij}-d_{0}}{s}\right)$$

Approach

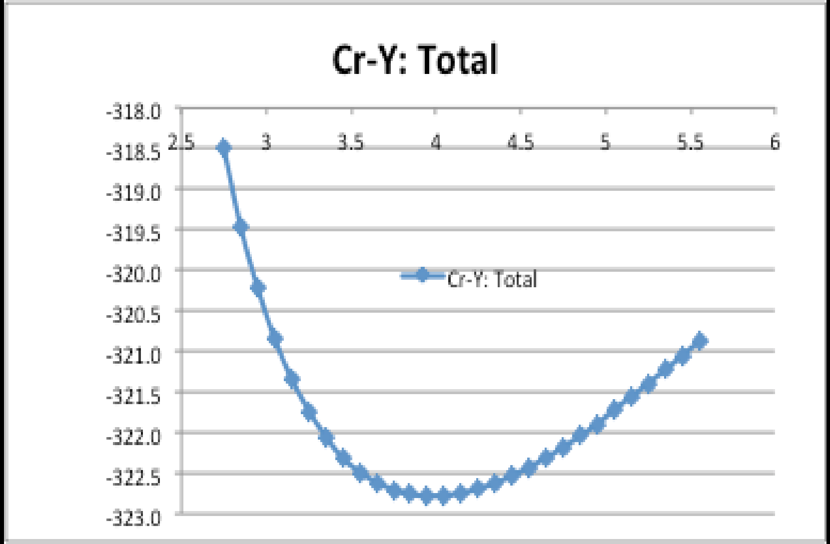
- By fitting the coefficients in UBER relation into the total energy equation, we can calculate the total energy of the system, thus the interatomic potential is known. Then classical like MD could be performed to simulate the physical properties.

- Advantages: Saving computer time while keep the accuracy similar to *ab initio* method.

Results of Cr-Y and Ta



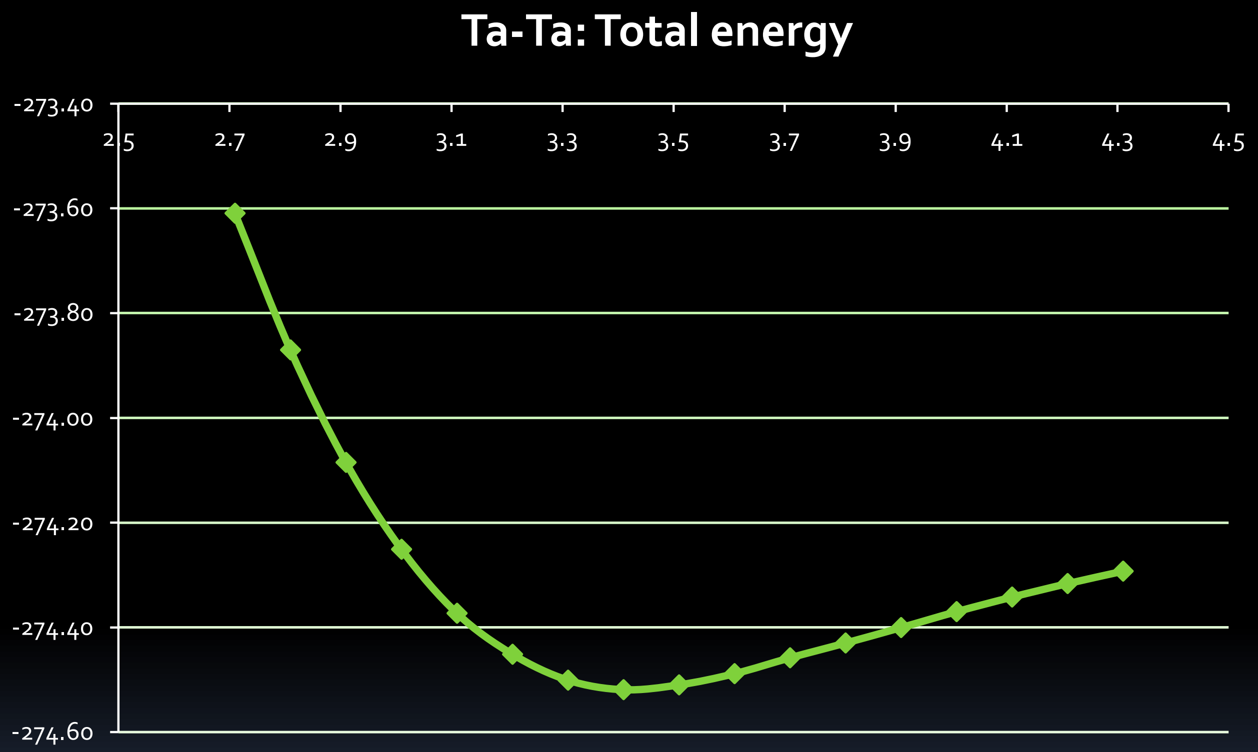
CrO (Fm3bm-FCC)



Cr-Y: Total

Cr-O and Cr-Y energy ~ lattice are close to experimental data and other simulation data.

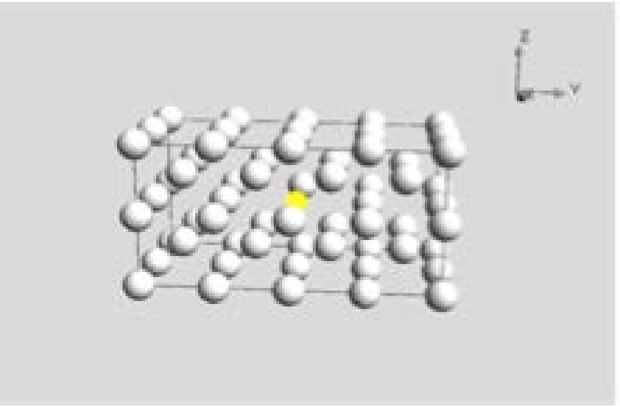
Results of Ta

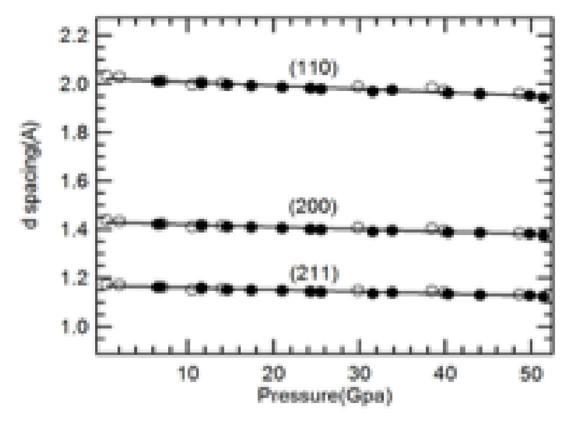


We have tested the Ta-Ta interatomic interaction. The energy ~ lattice result is close to experimental data. The final potential is under testing.

Results of Dilute Cr-Y

1. We had performed axial high pressure experiments (up to 42 GPa) on Cr-Y with wt 5% Y at LBNL beamline 12.2.2.
2. The data was analyzed and compared with our simulation results. The analysis shows that the Cr and Y metals are alloyed forming stable structure.



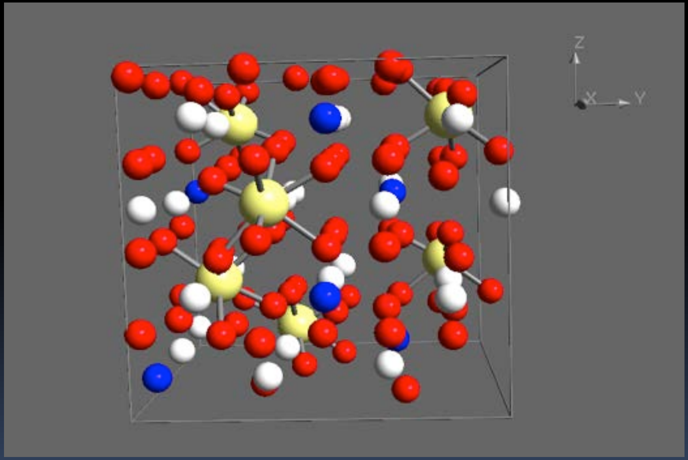


Results of Ta doped ZrO2

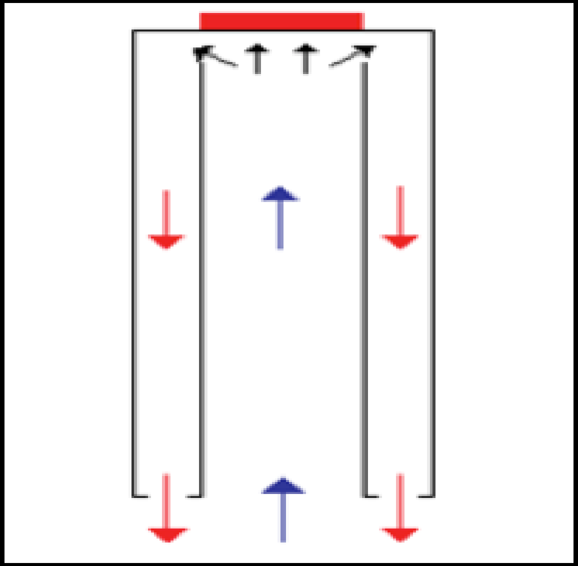
1. The MD simulation shows that the Ta:YSZ (Ta:Y=1:1) cubic structure is very stable even under high temperature over 1350°C.

2. The reflectivity at (111) direction reaches 65% at 10 eV.

Yellow ball: Ta atom
Blue ball: Y atom
White ball: Zr atom
Red ball: O atom



Thermal Cycling Testing Rig



- **Use Compressed Air to Produce Temperature Gradient**

Summary of Rig Test

- Thermal gradient cycling test combined high frequency cycling, rapid heating and cooling rate with 150°C temperature gradient was achieved.
- The long thermal cycling life of YSZ and double-ceramic-layered TBCs is attributed to the temperature gradient which makes the bond coat exposed at the designed working temperature (~950°C).
- At moderate surface temperature the functionally graded double layer 50%GZ/ YSZ TBC system meets the expectations, as the thermal cycling performance is similar to those of YSZ TBCs.

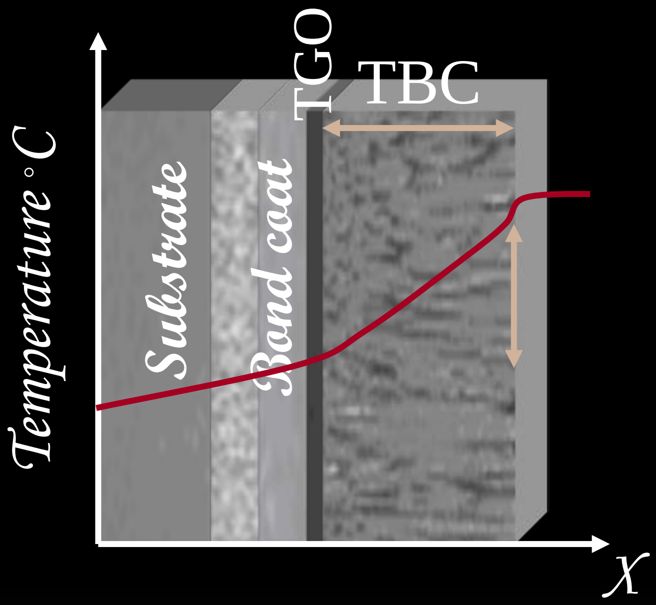
Results of YSZ, YSZ+$Gd_2Zr_2O_7$ and $Gd_2Zr_2O_7$ TBCs in Na_2SO_4+V_2O_5 at 1050°C

- HOT CORROSION is the result of accelerated oxidation at temperatures typically between 700°C and 925°C when metals and alloys become covered with contaminant salt films.
- Hot Corrosion Types :
  - Type I : occurs above the melting point of the salt, at the upper end of the temperature range.
  - Type II :
    - The corrosion at the lower end of the temperature range

Hot Corrosion

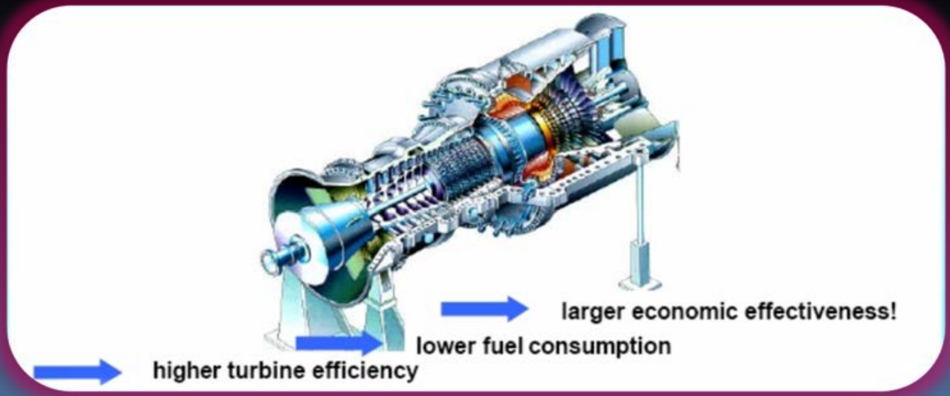
  - It may also occur above the salt melt temperature if the deposited salts form a eutectic mixture with the melting point significantly lower than that of the individual constituents.
  - These constituents include the product of reaction of the salts with the oxides formed on corroding metals and alloys.
- In both types of hot corrosion, fluxing with corroding salts defeats the protective oxide scale that forms on superalloys and coatings.
- The salts involved in hot corrosion are typically alkali and alkaline earth sulfates

Thermal Barrier coating



- The coatings enable metallic materials to be used at gas temperatures above their melting points.
- Thermal conductivity of the coating is the main factor of dropping temperature across the TBC.
- Provide enough insulation for superalloys to operate at temperatures as much as 150 °C above their customary upper limit.
- Efficiency can be increased in 5 – 8% through the use of ceramic TBCs

- Ceramic Top Coating
- Thermally grown oxide layer (TGO)
- Metalic bond coat layer
- Substrate



Zirconia Based TBCs

- Pure Zirconia
  - Melting Point = 2690°C
  - Zirconia assume three phases at different temperatures
    - Cubic (C) to tetragonal (T) = 2370 ° C
    - Tetragonal (T) to monoclinic (M) = 1170 °C
  - Tetragonal-to-monoclinic phase transformation is martensitic and involves a 3-5% volume increase
  - affecting the integrity of the coating.

- Alloying zirconia with other oxides such as CaO, MgO, Y_2O_3, CeO_2, Sc_2O_3, and In_2O_3
  - Inhibits the phase transformation
  - Stabilizes at high temperature
  - Eliminate the volume change

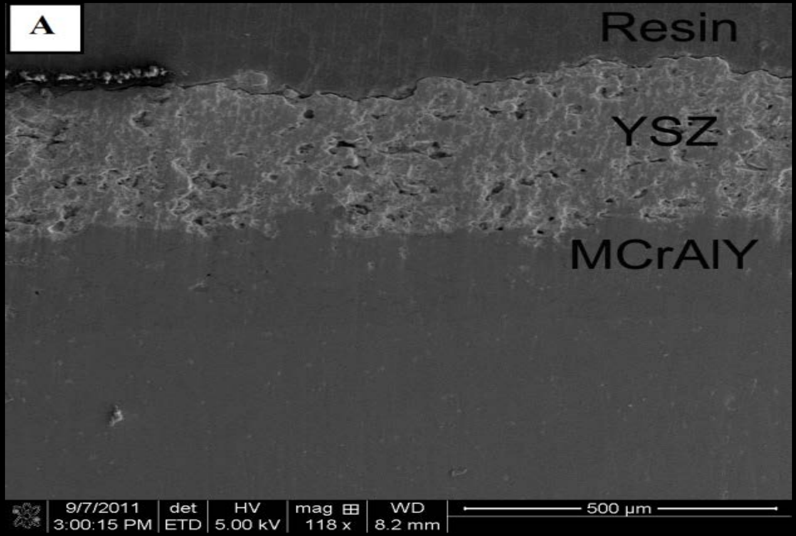
Rare-earth zirconate TBCs

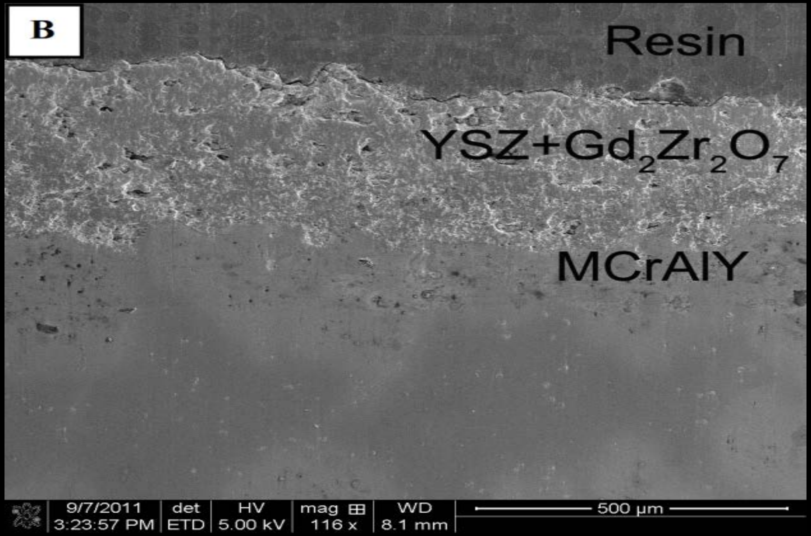
- The search for alternative coating materials other than the well established YSZ system has consisted of two main approaches:
  - (i) alternative materials to ZrO_2-based systems
  - (ii) alternative stabilizers to Y_2O_3 for ZrO_2-based systems.

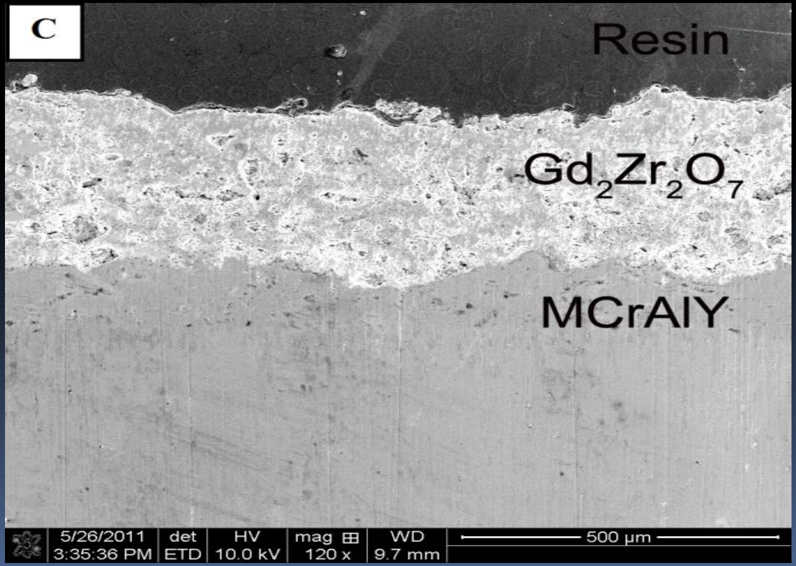
- Significantly, the $A_2B_2O_7$-type rare-earth zirconate ceramics, such as $La_2Zr_2O_7$, $Nd_2Zr_2O_7$, and $Gd_2Zr_2O_7$ and $Sm_2Zr_2O_7$, have been shown recently to have lower thermal conductivity, higher melting points, relatively higher thermal expansion coefficients (TEC), higher stability, and better ability to accommodate defects than YSZ.

- However, for the hot corrosion behavior of $Gd_2Zr_2O_7$ and other rare earth zirconates, most of early studies reported a temperature range between 650 to 900°C. In this Investigation, the hot corrosion behavior of $Gd_2Zr_2O_7$, YSZ, and $Gd_2Zr_2O_7$+YSZ composite coatings by $Na_2SO_4+V_2O_5$ mixture is examined at 1050°C.

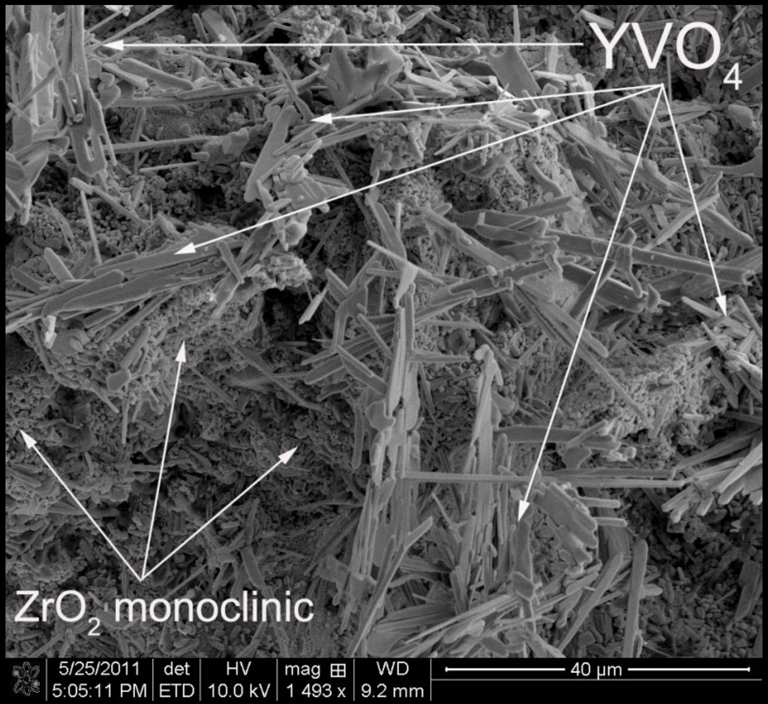
As received samples







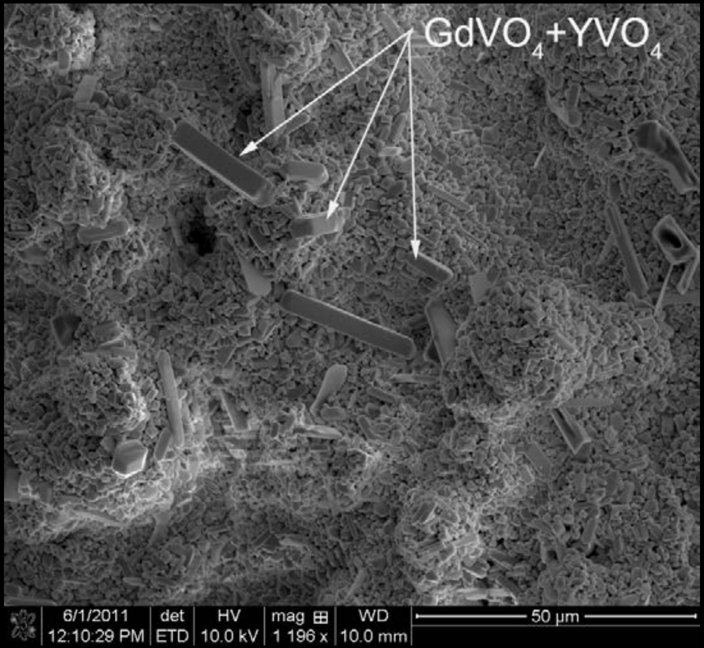
Hot corrosion Experiments

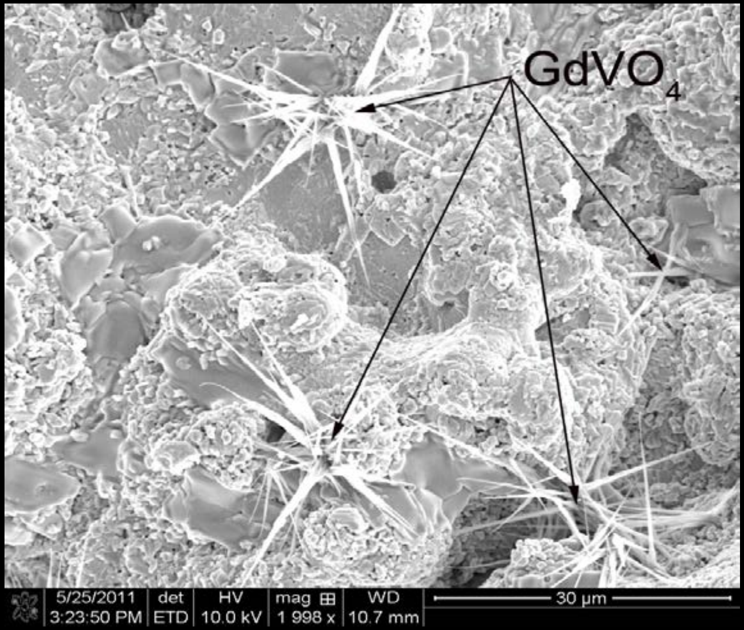


- Chemical degradation of conventional YSZ coatings can be classified as successive occurrence of related chemical reactions during the hot corrosion

- $V_2O_5 + Na_2SO_4 \longrightarrow 2\,(NaVO_3) + SO_3$
- $ZrO_2\,(Y_2O_3) + 2(NaVO_3) \longrightarrow ZrO_2 + 2(YVO_4) + Na_2O$

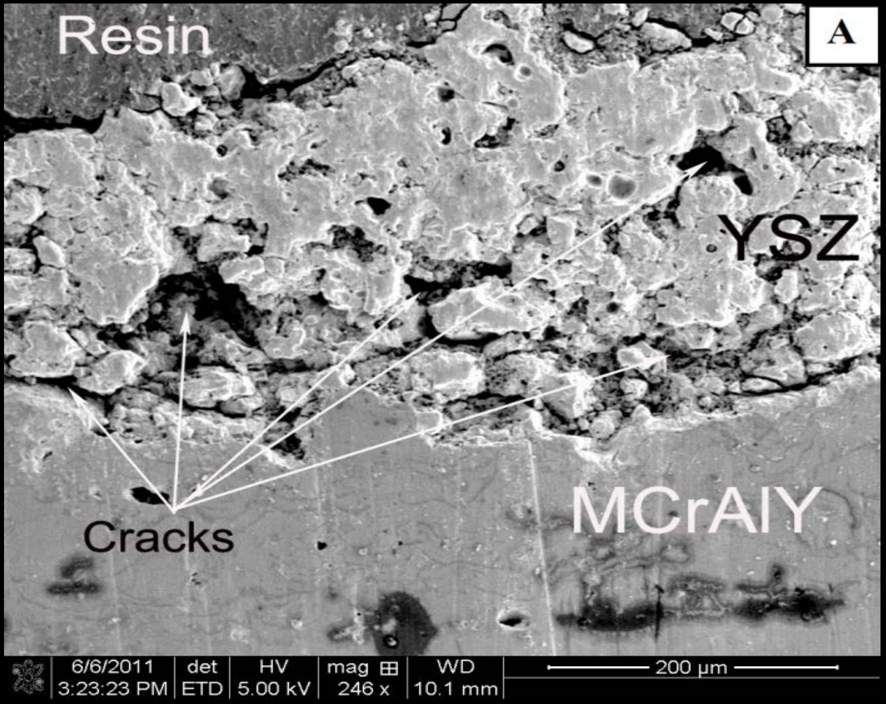
Hot corrosion Experiments





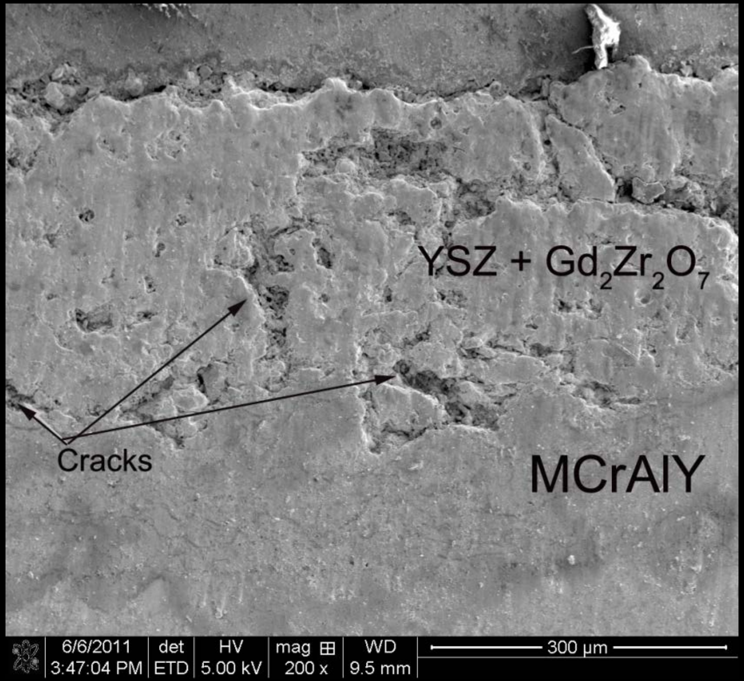
- Exposure of the $Gd_2Zr_2O_7$+YSZ and $Gd_2Zr_2O_7$ coatings to the molten mixture of $Na_2SO_4 + V_2O_5$ at 1050ºC
- $Gd_2Zr_2O_7(s) + 2\ NaVO_3\ (l) \longrightarrow 2GdVO_4(s) + 2ZrO_2$ (monoclinic) $+Na_2O$
- $Gd_2O_3(s) + 2NaVO_3\ (l) \longrightarrow GdVO_4(s) + Na_2O$

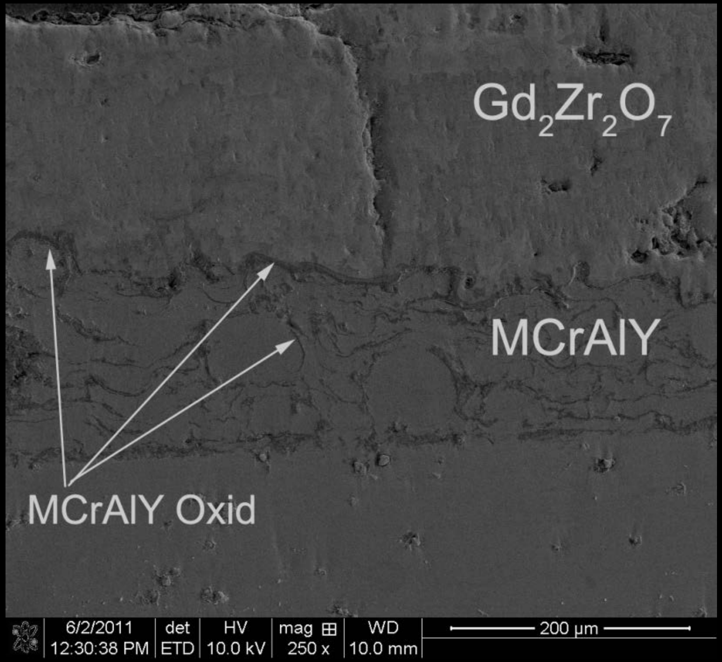
Hot corrosion Experiments



- large harmful horizontal cracks have formed inside the conventional YSZ layer throughout the thickness of coating.
- After losing Y_2O_3, the transformation of tetragonal zirconia to monoclinic zirconia during the cooling stage of thermal cycling is accompanied by 3-5% volume expansion, leading to cracking and spallation of TBCs.

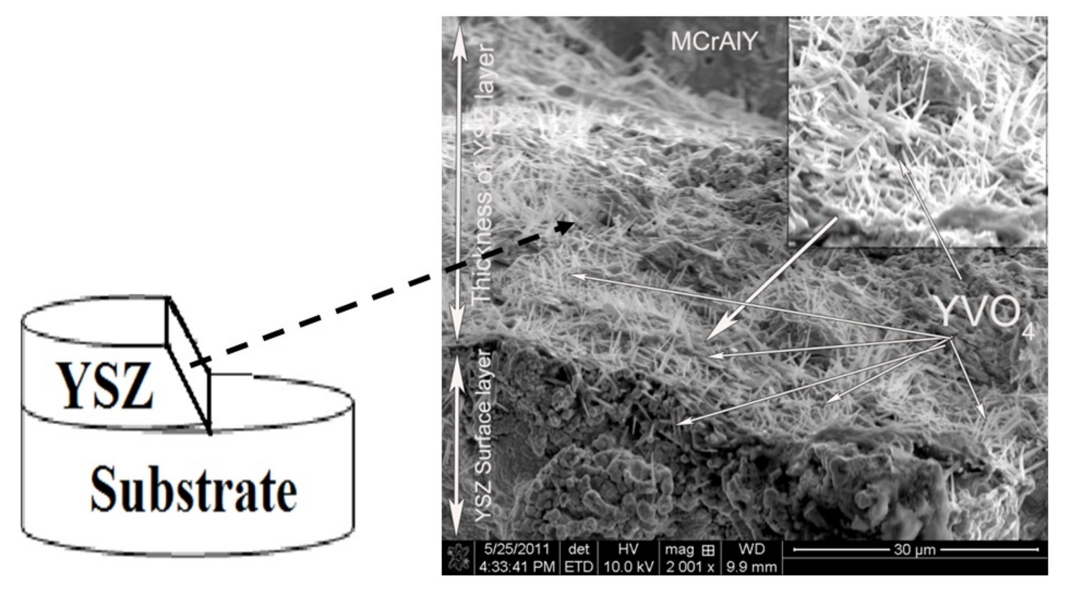
Hot corrosion Experiments





- In the case of $YSZ+Gd_2Zr_2O_7$ composite coatings, a few visible cracks were observed inside the zirconia layer after the hot corrosion test but no spallation was observed at the $YSZ+Gd_2Zr_2O_7$/bond coat interface which shows the integrity of coating after hot corrosion
- The right figure shows a $Gd_2Zr_2O_7$ coating cross-section, which has no significant degradation and spallation after hot corrosion

Hot corrosion Experiments



- During the exposure of V_2O_5 and Na_2SO_4 salt mixture at a high temperature (1050°C), a new compound of $NaVO_3$ may form

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

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

- The molten $NaVO_3$ is also reported to increase the atom mobility, hence further promote the depletion of yttria from YSZ and the growth of YVO_4 crystals After losing Y_2O_3, the transformation of tetragonal zirconia to monoclinic zirconia during the cooling stage of thermal cycling is accompanied by 3-5% volume expansion, leading to cracking and spallation of TBCs

Conclusions and Future work

- We confirmed that Y can be efficiently mechanically alloyed with Cr metal and stable under a stress up to 36 GPa.
- A strong hybridization is found among the 4p orbitals of Cr, 4d orbitals and 5p orbitals of Y.
- At nano-scale, the plastic deformation is found at (211) face.
- In Ta and Y 1:1 doped YSZ simulation, it is found that the cubic lattice structure is stable at a high temperature up to 1,350°C.

Conclusions and Future work

- The reactions between yttria (Y_2O_3) and V_2O_5 or $NaVO_3$ produce YVO_4, leaching Y_2O_3 from the YSZ and causing progressive tetragonal to monoclinic destabilization transformation.
- The production of $GdVO_4$ partially consumes V_2O_5 and thus postpones the formation of YVO_4 crystals and consequently less monoclinic ZrO_2 and less YVO_4 crystals are formed.
- The presence of fine-grained $Gd_2Zr_2O_7$ around YSZ particles also reduces the direct contact of conventional YSZ with molten salt, thus a better corrosion resistance. Molten $Na_2SO_4+V_2O_5$ mixture reacts with the bulk $Gd_2Zr_2O_7$ layer to form $GdVO_4$ and monoclinic ZrO_2.
- Under this accelerated hot corrosion test, bulk $Gd_2Zr_2O_7$ layer started to degrade after 36 hours of hot corrosion testing (9 cycles), which is much better than the YSZ case, which started to fail after 5 cycles, and the general status of the coating after hot corrosion, $Gd_2Zr_2O_7$ has a better hot corrosion resistance at a temperature of 1050°C than that of YSZ coatings.

Future work

- Continue to perform bond coat screening using MD method simulation to screen out the candidates.
- Screen out the top coat that matches the bond coat and remains stable under high temperature.
- Prepare and evaluate TBC systems identified in the simulation.

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