Computational Design and Experimental Validation of New Thermal Barrier Systems

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Outline

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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:

\[
E_{\text{total}}(\rho) = T + \sum_{lm} \int \rho(\vec{r}) d\vec{r} \left[ -\frac{e^2 Z_m}{|\vec{r} - \vec{r}_m - \vec{R}_l|} + \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} dv d\vec{r}' + E_{xc}(\rho) + \frac{1}{2} \sum_{mn} \frac{e^2 Z_m Z_n}{|\vec{r}_m - \vec{r}_n|}\right]
\]

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

\[
T \equiv E_{\text{rep}} = \frac{1}{2} \sum_{i,j}^{i \neq j} \varepsilon d_{ij}^n \exp\left(-\frac{d_{ij} - d_0}{s}\right)
\]
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

Cr-O and Cr-Y energy ~ lattice are close to experimental data and other simulation data.
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 ZrO$_2$

1. The MD simulation shows that the Ta:YSZ (Ta:Y=1:1) cubic structure is very stable even under high temperature over 1350$^\circ$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$_2$Zr$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$ TBCs in Na$_2$SO$_4$+V$_2$O$_5$ 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)
- Metallic 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.

- Alloyning zirconia with other oxides such as CaO, MgO, Y₂O₃, CeO₂, Sc₂O₃, and In₂O₃
  - 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$_2$O$_3$ for ZrO$_2$-based systems.

Significantly, the $A_2B_2O_7$-type rare-earth zirconate ceramics, such as La$_2$Zr$_2$O$_7$, Nd$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$, 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$_2$Zr$_2$O$_7$ and other rare earth zirconates, most of early studies reported a temperature range between 650 to 900ºC. In this Investigation, the hot corrosion behavior of Gd$_2$Zr$_2$O$_7$, YSZ, and Gd$_2$Zr$_2$O$_7$+YSZ composite coatings by Na$_2$SO$_4$+V$_2$O$_5$ mixture is examined at 1050ºC.
As received samples

A

Resin

YSZ

MCrAIY

B

Resin

YSZ + Gd₂Zr₂O₇

MCrAIY

C

Resin

Gd₂Zr₂O₇

MCrAIY
Hot corrosion Experiments

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

- \( V_2O_5 + Na_2SO_4 \rightarrow 2(NaVO_3) + SO_3 \)
- \( ZrO_2(Y_2O_3) + 2(NaVO_3) \rightarrow ZrO_2 + 2(YVO_4) + Na_2O \)
Hot corrosion Experiments

- Exposure of the Gd$_2$Zr$_2$O$_7$ + YSZ and Gd$_2$Zr$_2$O$_7$ coatings to the molten mixture of Na$_2$SO$_4$ + V$_2$O$_5$ at 1050°C

- Gd$_2$Zr$_2$O$_7$(s) + 2 NaVO$_3$ (l) $\rightarrow$ 2GdVO$_4$(s) + 2ZrO$_2$ (monoclinic) + Na$_2$O

- Gd$_2$O$_3$(s) + 2NaVO$_3$ (l) $\rightarrow$ GdVO$_4$(s) + Na$_2$O
Hot corrosion Experiments

- Large harmful horizontal cracks have formed inside the conventional YSZ layer throughout the thickness of coating.
- After losing $\text{Y}_2\text{O}_3$, 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.
In the case of YSZ+Gd$_2$Zr$_2$O$_7$ 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$_2$Zr$_2$O$_7$/bond coat interface which shows the integrity of coating after hot corrosion.

The right figure shows a Gd$_2$Zr$_2$O$_7$ coating cross-section, which has no significant degradation and spallation after hot corrosion.
During the exposure of V$_2$O$_5$ and Na$_2$SO$_4$ 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$_2$O$_3$, 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$_2$O$_3$) and V$_2$O$_5$ or NaVO$_3$ produce YVO$_4$, leaching Y$_2$O$_3$ from the YSZ and causing progressive tetragonal to monoclinic destabilization transformation.
- The production of GdVO$_4$ partially consumes V$_2$O$_5$ 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$_2$Zr$_2$O$_7$ around YSZ particles also reduces the direct contact of conventional YSZ with molten salt, thus a better corrosion resistance. Molten Na$_2$SO$_4$ + V$_2$O$_5$ mixture reacts with the bulk Gd$_2$Zr$_2$O$_7$ layer to form GdVO$_4$ and monoclinic ZrO$_2$.
- Under this accelerated hot corrosion test, bulk Gd$_2$Zr$_2$O$_7$ 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$_2$Zr$_2$O$_7$ 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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