



Thermochemistry of Protective Coatings and Molten Silicate Debris

Gustavo Costa^{1*}, Bryan Harder¹, Benjamin Kowalski¹,
Narottam Bansal¹, Jamesa Stokes^{1,2}, Sergey Ushakov³,
Alexandra Navrotsky³

¹NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, OH,
44135, USA

^{1*}Vantage Partners, LLC

²Department of Materials Science and Engineering, The Pennsylvania State
University, University Park, PA 16801, USA

³Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of
California Davis, Davis, CA 95616, USA



Outline of Presentation

- Ceramic Coating Materials
- Experimental Thermodynamics
 - Integral thermodynamic quantities: High Temperature Reaction Calorimetry
- Rare earth Silicates and Zirconia based Coatings Exposed to Mineral Dust Particles (CMAS) and High Temperature Calorimetry
- Enthalpies of Formation of Calcium Rare-earth Silicate Oxyapatites and High Temperature Drop Solution Calorimetry (AlexSys)



Ceramic Coating Materials

- Thermal Barrier Coatings (TBCs): Reduce heat flux towards the underlining material
7YSZ, 31YSZ, 16RESZ (RE = Y, Gd and Yb), $Gd_2Zr_2O_7$
- Environmental Barrier Coatings (EBCs): Barrier to chemically corrosive agents
 $Y_2Si_2O_7$ and $Yb_2Si_2O_7$



Experimental Thermodynamics: High Temperature Calorimetry

1. Coating Materials - Mineral Dust Particles

HT Drop Solution Calorimetry @ 1500 °C

-coating materials dropped into the calorimeter containing molten silicate debris solvent
(CaO-MgO-Al₂O₃-SiO₂ or CMAS)

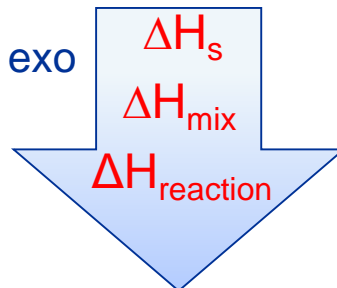
$$\Delta H_{ds} = \Delta H_{TTD} + \Delta H_s \quad \begin{matrix} \nearrow \\ \text{DnC} \\ \text{DTA} \end{matrix}$$

$$\Delta H_s = \Delta H_{mix} + \Delta H_{fusion}$$

$$\Delta H_{reaction} = n\Delta H_{s, coating} - n\Delta H_{s, reaction products}$$

- Process is favored: more exo (negative) or less endo (positive)

- Coating selection



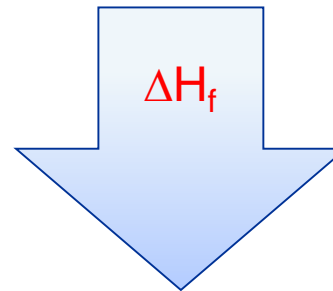
2 - Calcium Rare-earth Silicate Oxyapatites

HT Drop Solution Calorimetry @ 805 °C

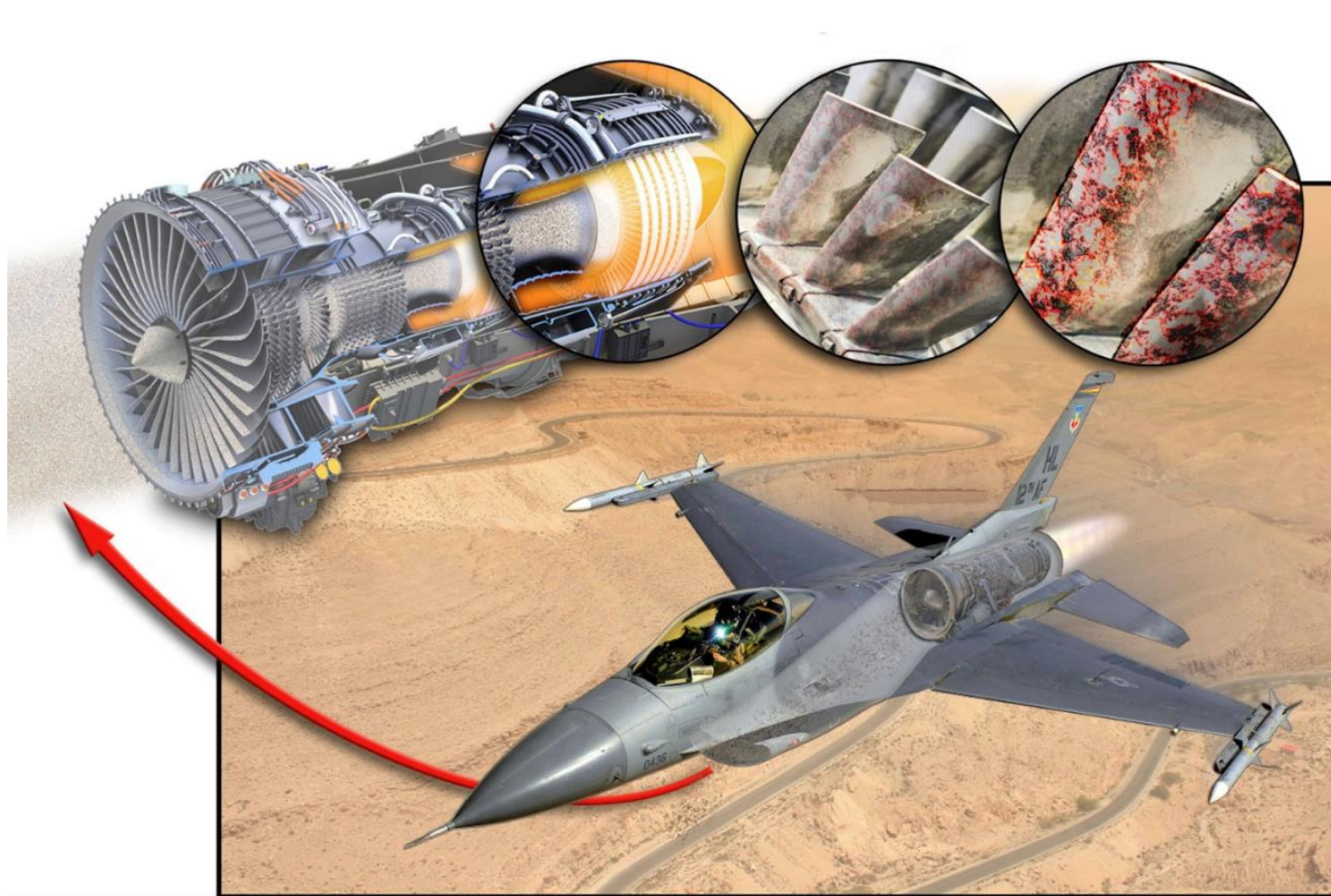
-Calcium rare-earth silicate oxyapatites dropped into the calorimeter containing lead borate solvent

ΔH_f for Ca₂RE₈Si₆O₂₆ (Y, Nd, Sm, Gd, Dy, Er, and Yb); main corrosion product between CMAS and coating materials

- Stability increases: more exo (negative)
-Input into thermodynamic codes



Rare earth Silicates and Zirconia based Coating Materials Exposed to **Mineral Dust Particles** **(CMAS)** and High Temperature Calorimetry



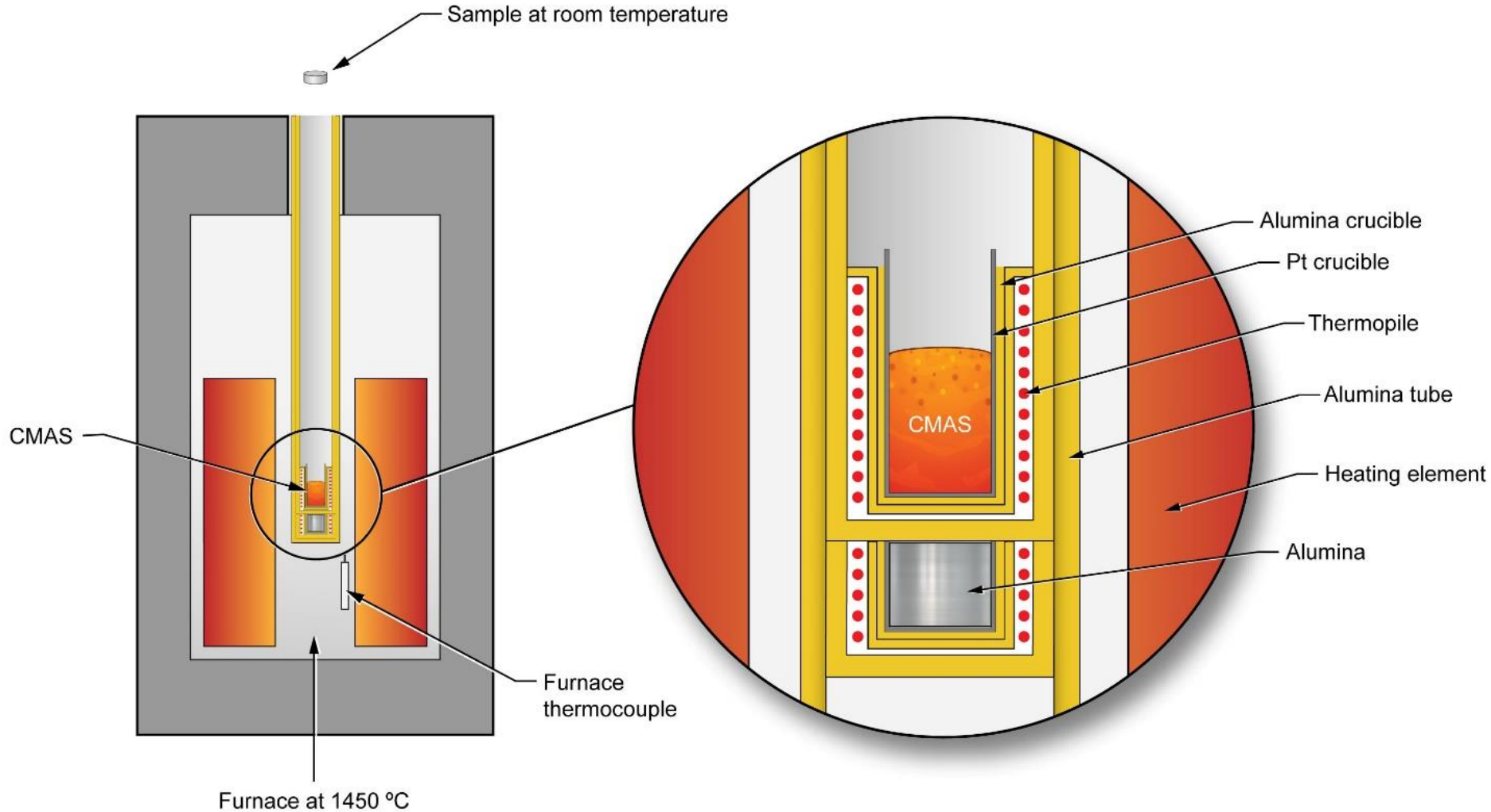


Rare earth Silicates and Zirconia based Coatings Exposed to **Mineral Dust Particles (CMAS)** and High Temperature Calorimetry

- Collaboration between NASA GRC and University of California, Davis (Prof. Alexandra Navrotsky)
- Combination of three calorimetric techniques and High Temperature X-ray diffraction
 1. High Temperature Solution Calorimetry – uses molten CMAS as a solvent
 2. Drop-and-catch (DnC) calorimetry
 3. Differential thermal analysis (DTA)
- Coating Materials
 - TBCs – 7YSZ, 31YSZ, 16RESZ (RE = Y, Gd and Yb), $Gd_2Zr_2O_7$
 - EBCs – $Y_2Si_2O_7$ and $Yb_2Si_2O_7$
- Reaction Products
 - Apatites - $CaY_4Si_3O_{13}$ and $CaYb_4Si_3O_{13}$
- CMAS with varying Ca/Si (0.27, 0.48 and 0.71)

High Temperature Solution Calorimetry

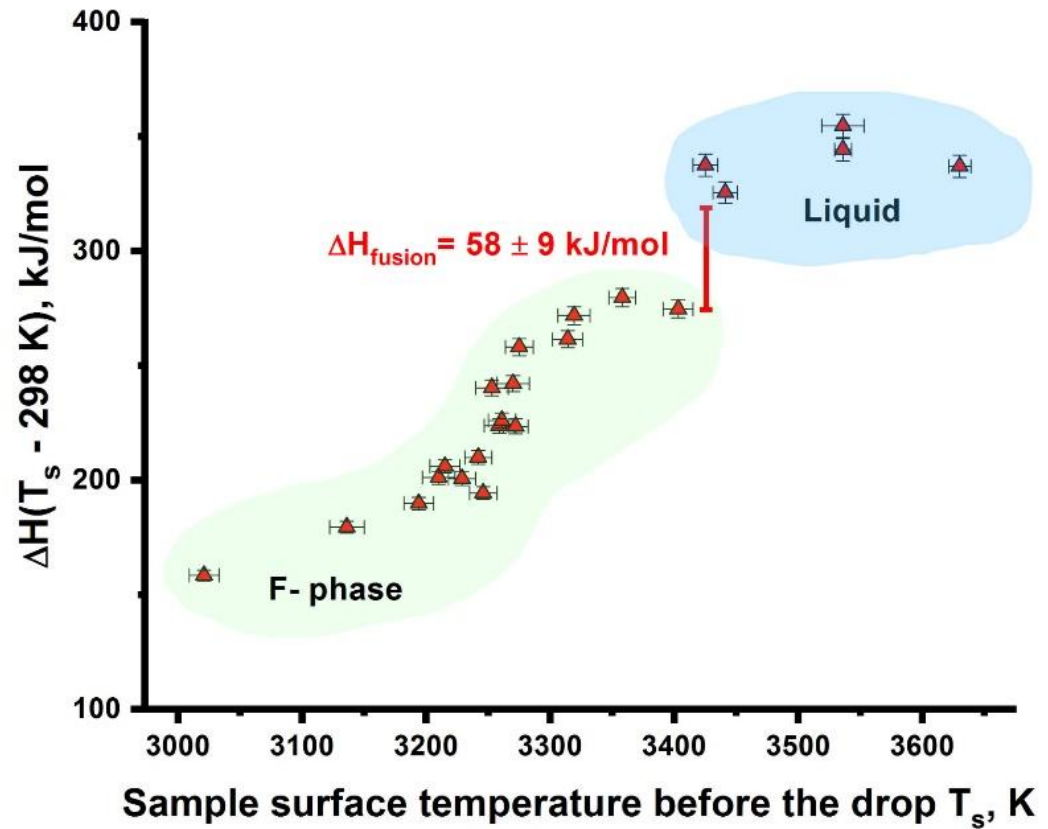
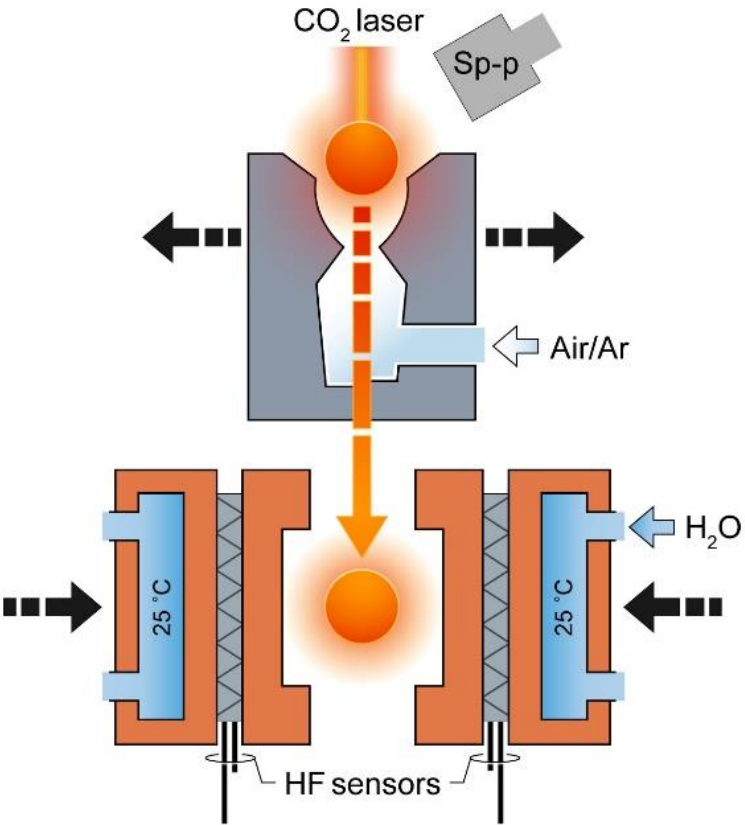
Setaram MHTC-96 – UC Davis



$$\Delta H_{ds} = \Delta H_{TTD} + \Delta H_s \left\{ \begin{array}{l} \Delta H_{\text{reaction}} \text{ assuming apatite formation} \\ \Delta H_{\text{mix}} \text{ knowing } \Delta H_{\text{fusion}} \end{array} \right.$$

Drop-and-Catch (DnC) Calorimetry

Designed and built at UC Davis



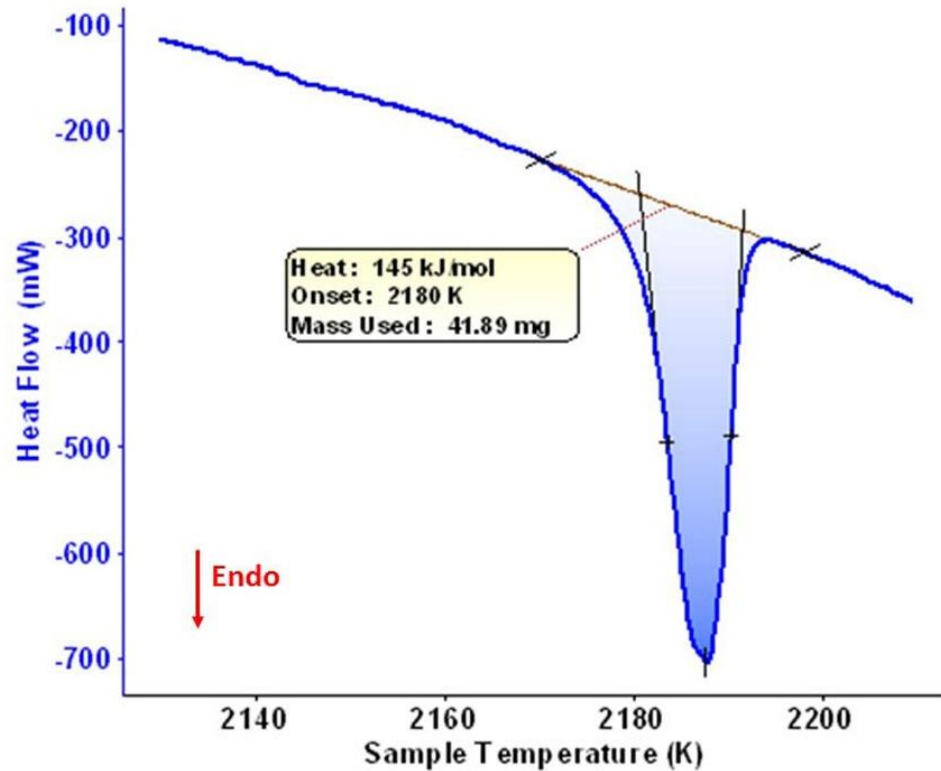
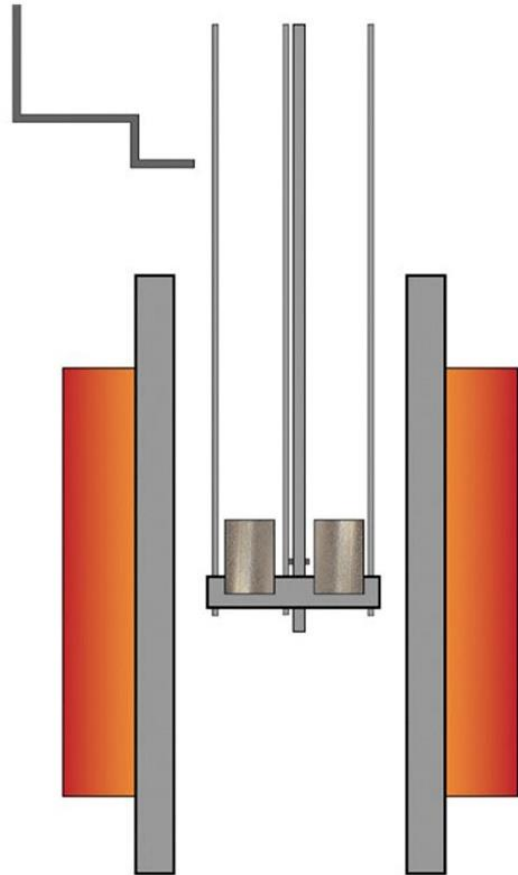
$$\Delta H_{\text{mix}} = \Delta H_s - \Delta H_{\text{fusion}}$$

High Temperature Solution Calorimeter

DnC on 7YSZ sample

Differential Thermal Analysis (DTA)

Setaram Setsys Evolution – UC Davis



$$\Delta H_{\text{mix}} = \Delta H_{\text{s}} - \Delta H_{\text{fusion}}$$

High Temperature Solution Calorimeter

DTA on $\text{Yb}_2\text{Si}_2\text{O}_7$ and $\text{CaYb}_4\text{Si}_3\text{O}_{13}$



Calorimetric Results

ΔH_{mix} and ΔH_{s} \rightarrow Process is more favored: more exo (negative) or less endo (positive)

Enthalpies of solution of the coating materials and apatites measured by high temperature calorimetry in molten CMAS at 1723 K.

Material in CMAS (0.71 Ca/Si)	Avg. reaction time (min)	ΔH_{s} (kJ/g-atom)
7YSZ	7	-4.78 \pm 1.14
16RESZ	15	12.71 \pm 1.41
31YSZ	20	17.86 \pm 1.51
Gd ₂ Zr ₂ O ₇	10	-7.59 \pm 0.65
Y ₂ Si ₂ O ₇	9	19.46 \pm 2.88
Yb ₂ Si ₂ O ₇	11	12.38 \pm 0.65
CaY ₄ Si ₃ O ₁₃	8	4.78 \pm 1.00
CaYb ₄ Si ₃ O ₁₃	7	11.57 \pm 0.72

Ca/Si	Y ₂ Si ₂ O ₇	Yb ₂ Si ₂ O ₇	Gd ₂ Zr ₂ O ₇
0.71	19.46 \pm 2.88	12.38 \pm 0.65	-7.59 \pm 0.65
0.48	7.98 \pm 1.69	11.45 \pm 1.79	-4.35 \pm 1.00
0.27	5.50 \pm 1.58	8.92 \pm 0.62	-4.40 \pm 0.56

Enthalpies and entropies of fusion of the coating materials, and enthalpies of mixing between molten CMAS and the coating materials at 1723 K.

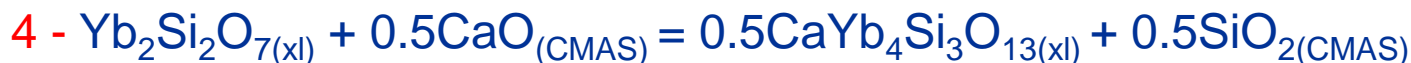
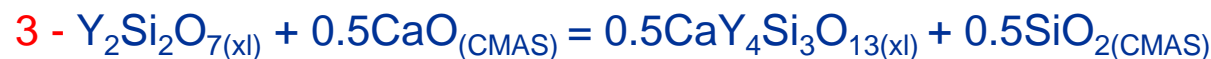
Material	$\Delta H_{\text{fusion}}^*$ (kJ/g-atom)	ΔH_{mix} (kJ/g-atom)
7YSZ	19.73 \pm 3.06	-24.51 \pm 3.27
Yb ₂ Si ₂ O ₇	13.73 \pm 0.73	-1.35 \pm 0.98
CaYb ₄ Si ₃ O ₁₃	11.43 \pm 0.52	0.14 \pm 0.89



Calorimetric Results

$\Delta H_{\text{reaction}}$ \rightarrow Process is favored: more exo (negative) or less endo (positive)

Enthalpies of reaction between the coatings and CMAS melt assuming apatite formation at 1723 K

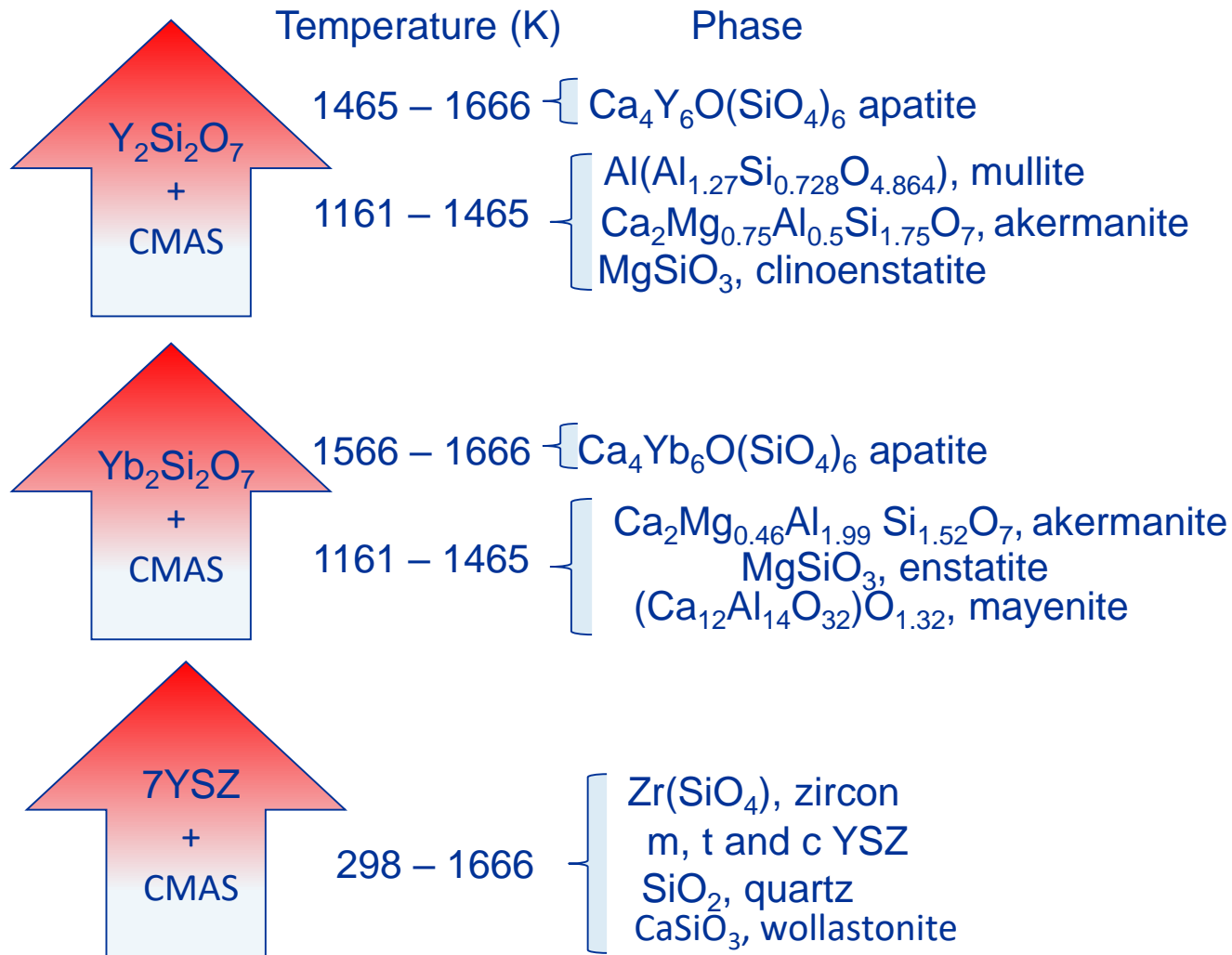


Enthalpy change	$\Delta H_{\text{reaction}}$ (kJ/g-atom)
$\Delta H_1 = \Delta H_{\text{sol}}(\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94(\text{xl}), 1450^\circ\text{C}}) - 0.03 \Delta H_{\text{sol}}(\text{CaY}_4\text{Si}_3\text{O}_{13(\text{xl}), 1723 \text{ K}})$	-4.92 ± 1.14
$\Delta H_2 = \Delta H_{\text{sol}}(\text{Zr}_{0.53}\text{Y}_{0.47}\text{O}_{1.77(\text{xl}), 1450^\circ\text{C}}) - 0.1175 \Delta H_{\text{sol}}(\text{CaY}_4\text{Si}_3\text{O}_{13(\text{xl}), 1723 \text{ K}})$	17.30 ± 1.51
$\Delta H_3 = \Delta H_{\text{sol}}(\text{Y}_2\text{Si}_2\text{O}_{7(\text{xl}), 1450^\circ\text{C}}) - 0.5 \Delta H_{\text{sol}}(\text{CaY}_4\text{Si}_3\text{O}_{13(\text{xl}), 1723 \text{ K}})$	17.07 ± 2.92
$\Delta H_4 = \Delta H_{\text{sol}}(\text{Yb}_2\text{Si}_2\text{O}_{7(\text{xl}), 1450^\circ\text{C}}) - 0.5 \Delta H_{\text{sol}}(\text{CaYb}_4\text{Si}_3\text{O}_{13(\text{xl}), 1723 \text{ K}})$	6.60 ± 0.74



High temperature X-ray diffraction

Crystalline phases detected during heating of ceramic material coatings and NASA CMAS powder mixture up to 1666 K.





Summary

Rare-Earth Silicates and Zirconia based coatings

- Enthalpies of solution for YDS, YbDS, Y and Yb – apatites, 16RESZ and 31YSZ are moderately positive except for 7YSZ and $Gd_2Zr_2O_7$
- Enthalpies of solution of YDS and YbDS becomes less endothermic with decreasing Ca/Si while an opposite trend is observed for $Gd_2Zr_2O_7$
- Apatite formation is only favorable over coating dissolution in terms of enthalpy for 7YSZ
- Mixing Enthalpies of YbDS and Yb apatite are less exothermic than 7YSZ
- The energetics for apatite formation in the case of silicates is favorable when other intermediate phases are present
 - $Y_2Si_2O_7$ - CMAS reaction, akermanite, mullite and clinoenstatite were detected between 1161 and 1465 K
 - $Yb_2Si_2O_7$ - CMAS reaction, akermanite, enstatite and mayenite were detected between 1161 and 1465 K prior to the detection of apatite at 1566 K.

Energetics of Calcium Rare-earth Silicate Oxyapatites



Corrosion product of Ceramic Coatings

$\text{Ca}_2\text{RE}_8\text{Si}_6\text{O}_{26}$ (Y, Nd, Sm, Gd, Dy, Er, and Yb)

Rare – earth silicates (EBCs) + silicate debris (CMAS) = Rare-earth silicate oxyapatites

${}^{\text{IX}}\text{M}(1)_4{}^{\text{VII}}\text{M}(2)_6({}^{\text{IV}}\text{TO}_4)_6\text{X}_2$ – generic formula

M – Rare-earth or alkaline earth

X – mono or divalent anions

T – p - block element

Superscript – coordination number

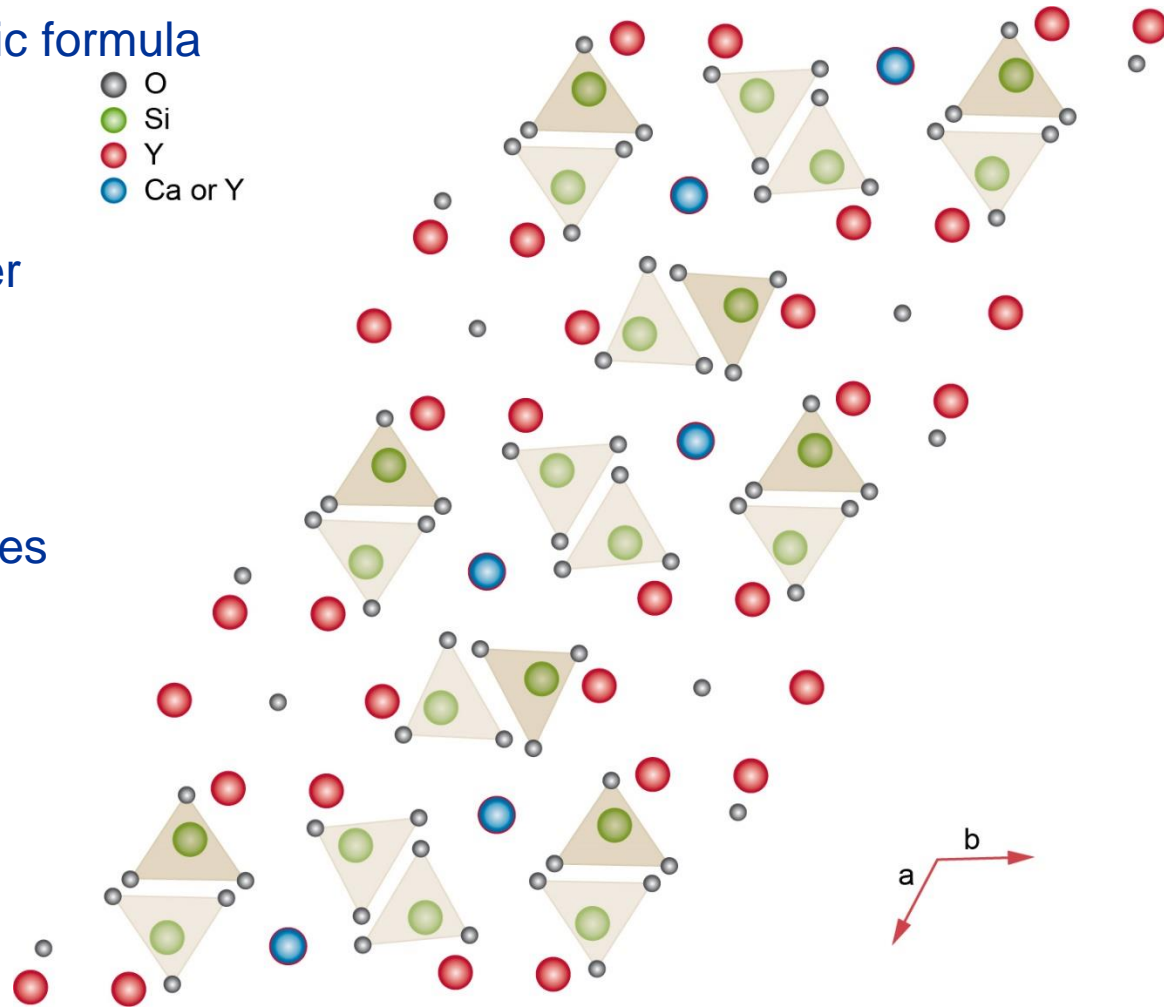


$\text{RE}_{10}\text{Si}_6\text{O}_{27}$ – interstitial oxygen

$\text{RE}_{9.33}\square_{0.67}\text{Si}_6\text{O}_{26}$ – cation vacancies

$\text{RE}_8\text{AE}_2\text{Si}_6\text{O}_{26}$ – stoichiometric

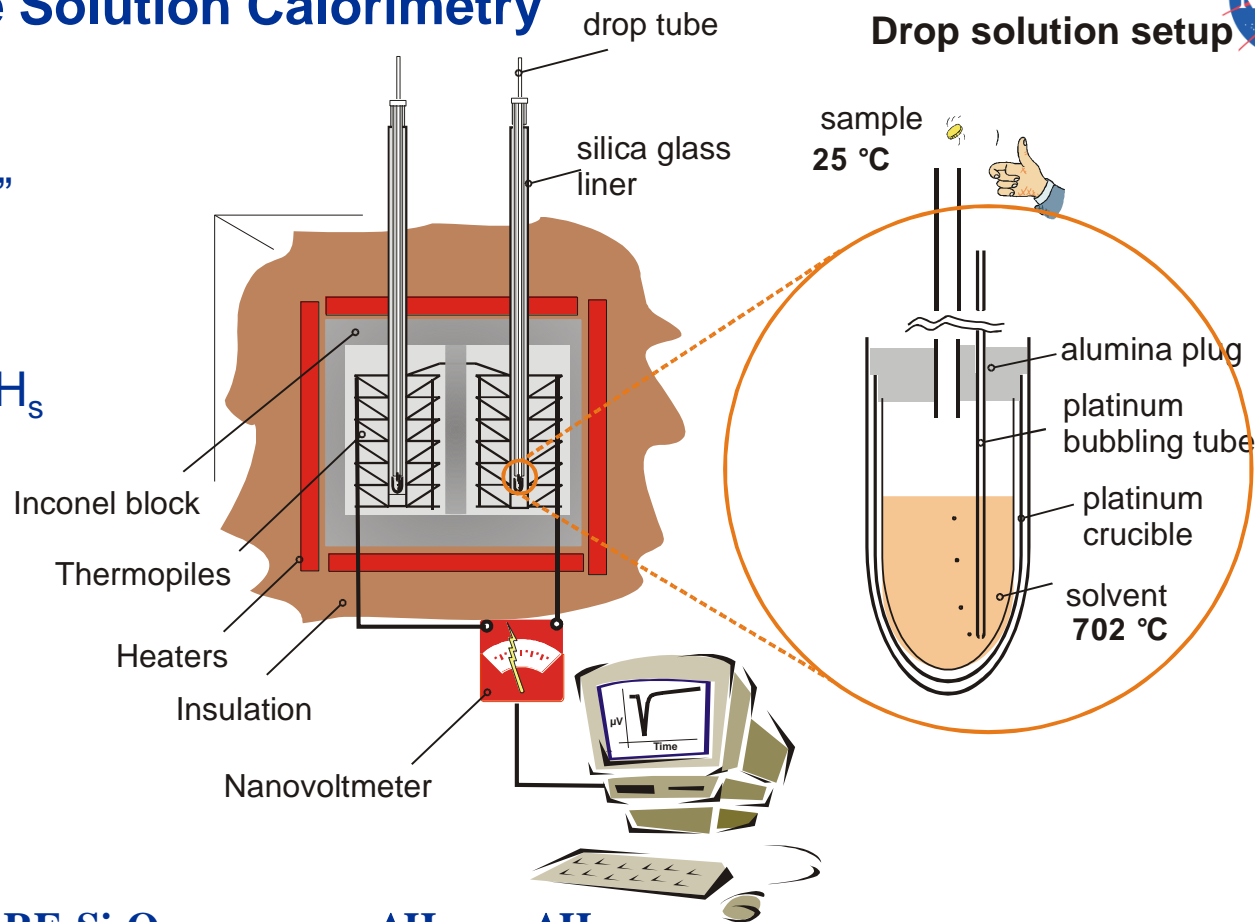
AE – alkaline earth



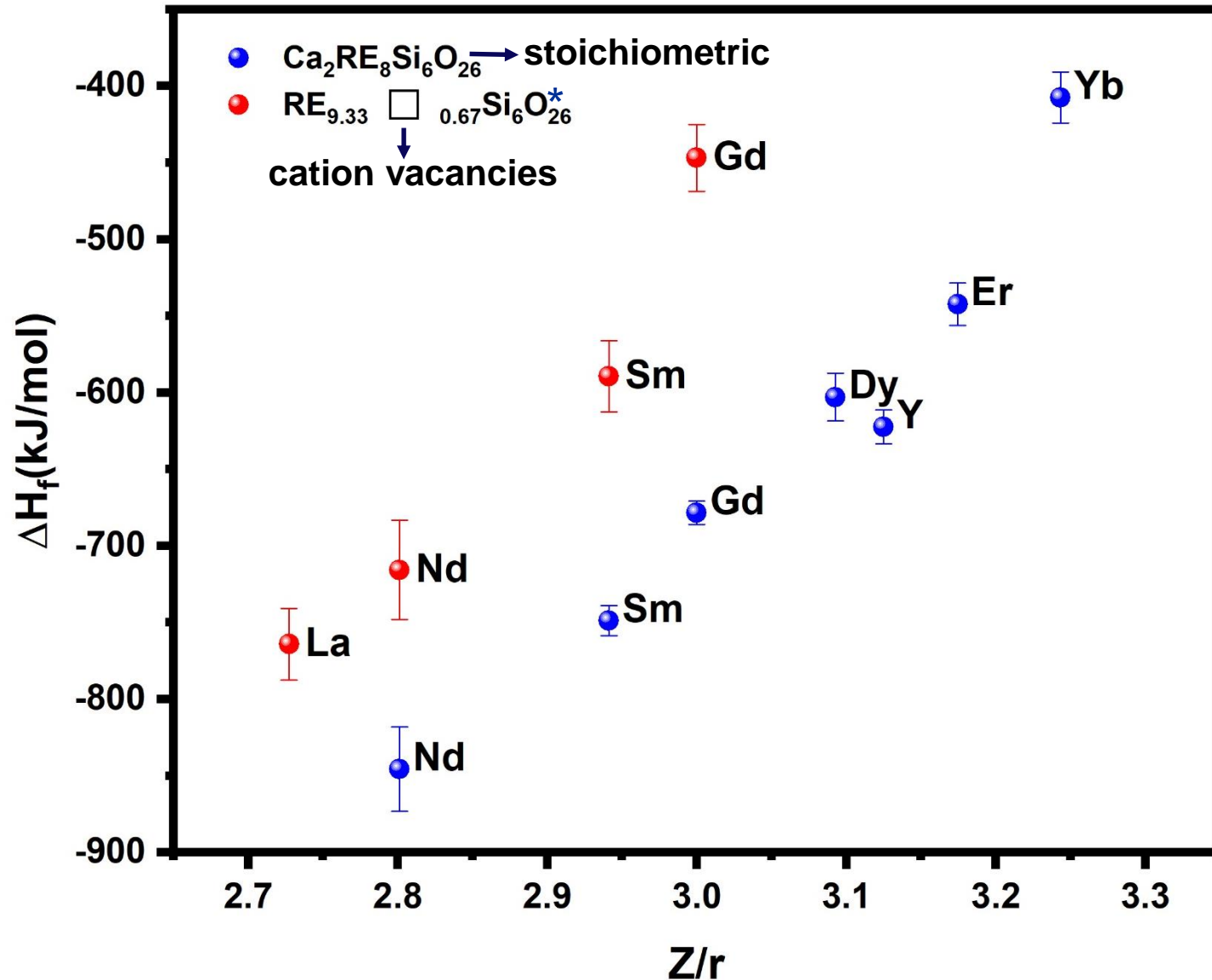
High Temperature Solution Calorimetry

Setaram "AlexSys"
NASA GRC

$$\Delta H_{ds} = \Delta H_{TTD} + \Delta H_s$$



Calorimetric Results



Enthalpy of formation of the Rare – earth silicate oxyapatites Versus their ionic potential (Z/r)



Summary

Calcium Rare-earth Apatites

- Apatites are significantly more stable relative to their binary oxides
- Calcium RE silicate oxyapatites are more stable than the RE oxyapatites with cation vacancies
- Apatite phases become more stable as the ionic potential decreases or the ionic radius become larger