Thermochemistry of Aerospace Materials

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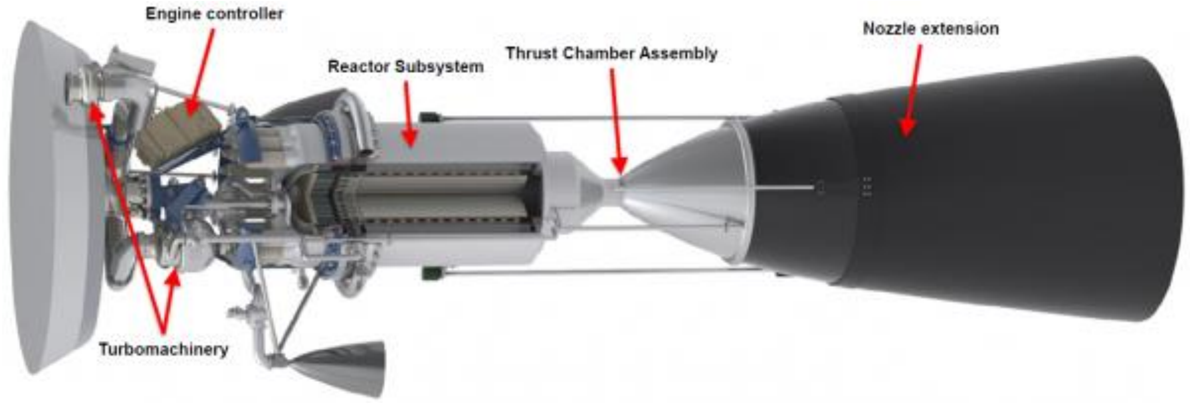
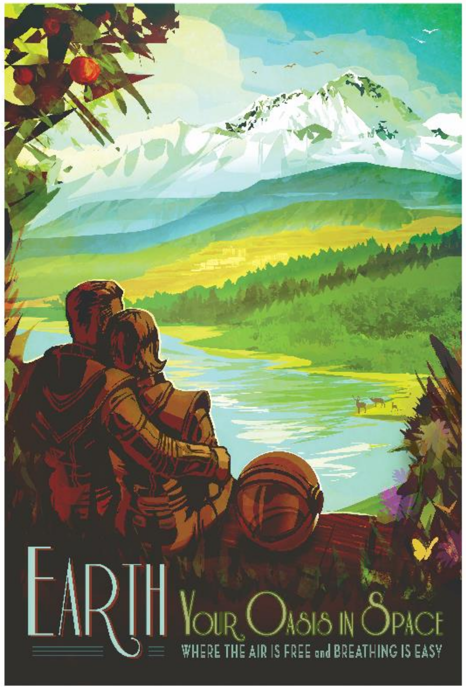
Aerospace Propulsion

Nuclear Thermal Propulsion (NTP)



Chemical Propulsion

Interplanetary transportation



- ***Key Factors: Efficiency and time***
- ***Main limited technical factor: “Propulsion”***

https://www.jpl.nasa.gov/visions-of-the-future/

Nuclear Thermal Propulsion (NTP)

-Highest mass specific energy sources at atomic level

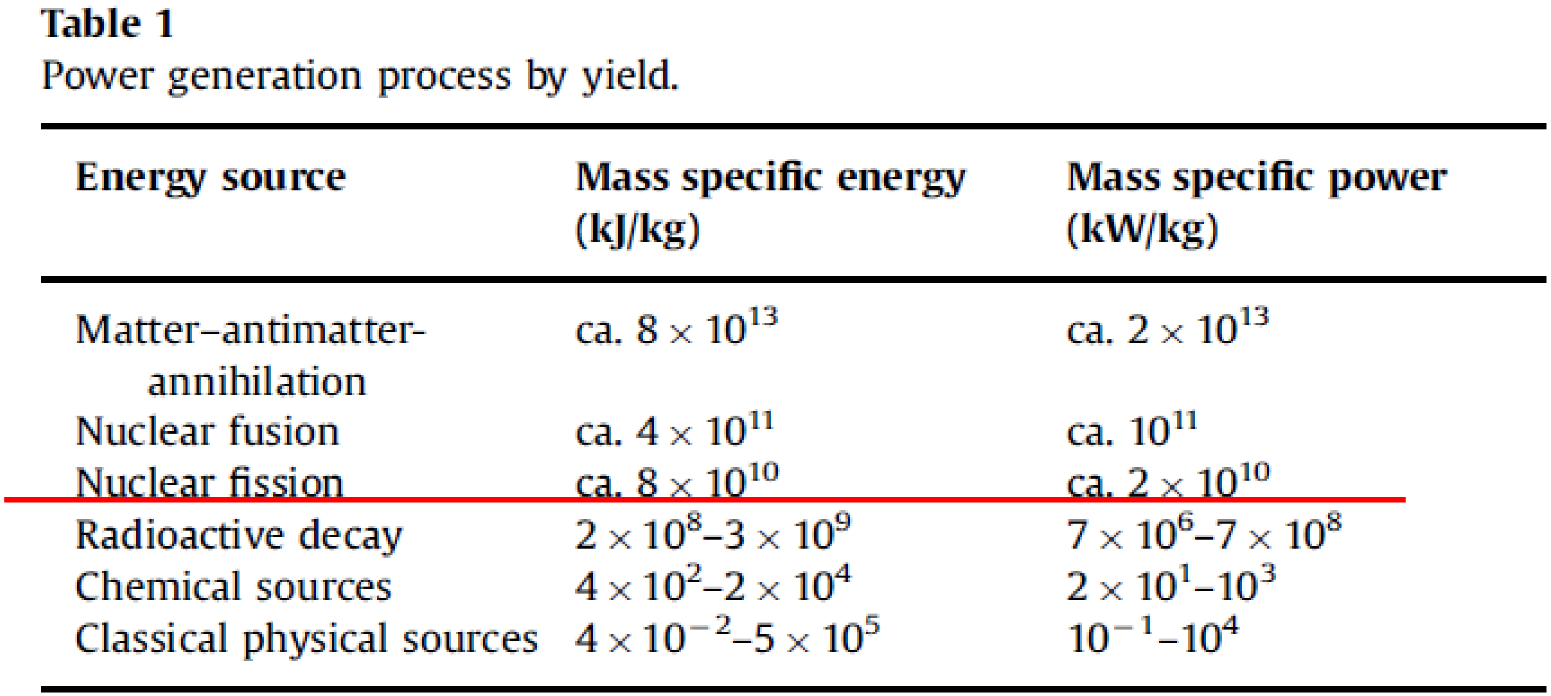
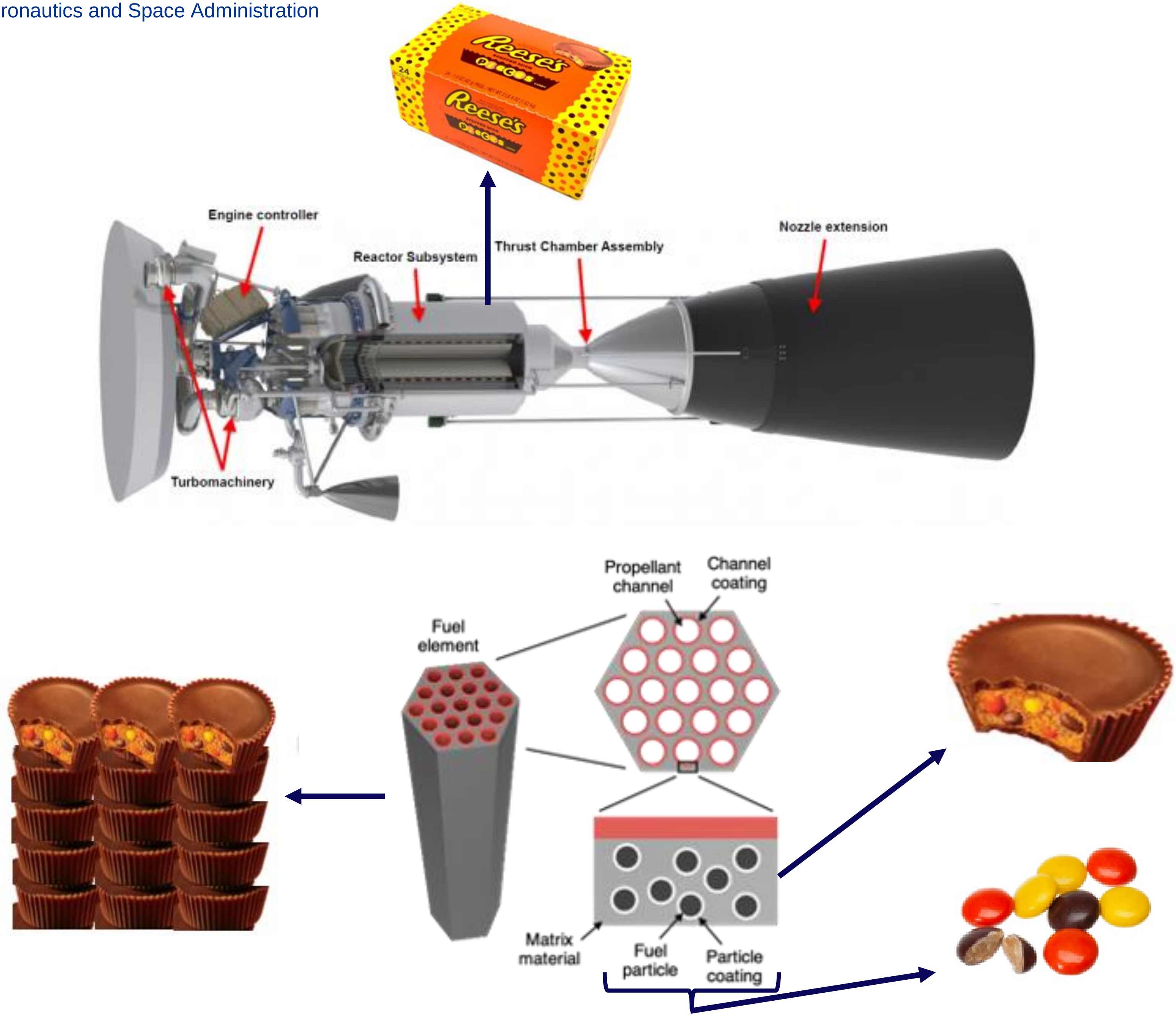


Table 1

Power generation process by yield.

Energy source	Mass specific energy (kJ/kg)	Mass specific power (kW/kg)
Matter–antimatter-annihilation	ca. 8×10^{13}	ca. 2×10^{13}
Nuclear fusion	ca. 4×10^{11}	ca. 10^{11}
Nuclear fission	ca. 8×10^{10}	ca. 2×10^{10}
Radioactive decay	2×10^{8}–3×10^{9}	7×10^{6}–7×10^{8}
Chemical sources	4×10^{2}–2×10^{4}	2×10^{1}–10^{3}
Classical physical sources	4×10^{-2}–5×10^{5}	10^{-1}–10^{4}

Gabrielli & Herdrich, Progress in Aerospace Sciences 79, 91-113, 2015.



https://www1.grc.nasa.gov/research-and-engineering/nuclear-thermal-propulsion-systems/; Tucker et al, Nuclear Technology, 207, 6, 2021.

Thermochemical Calculations

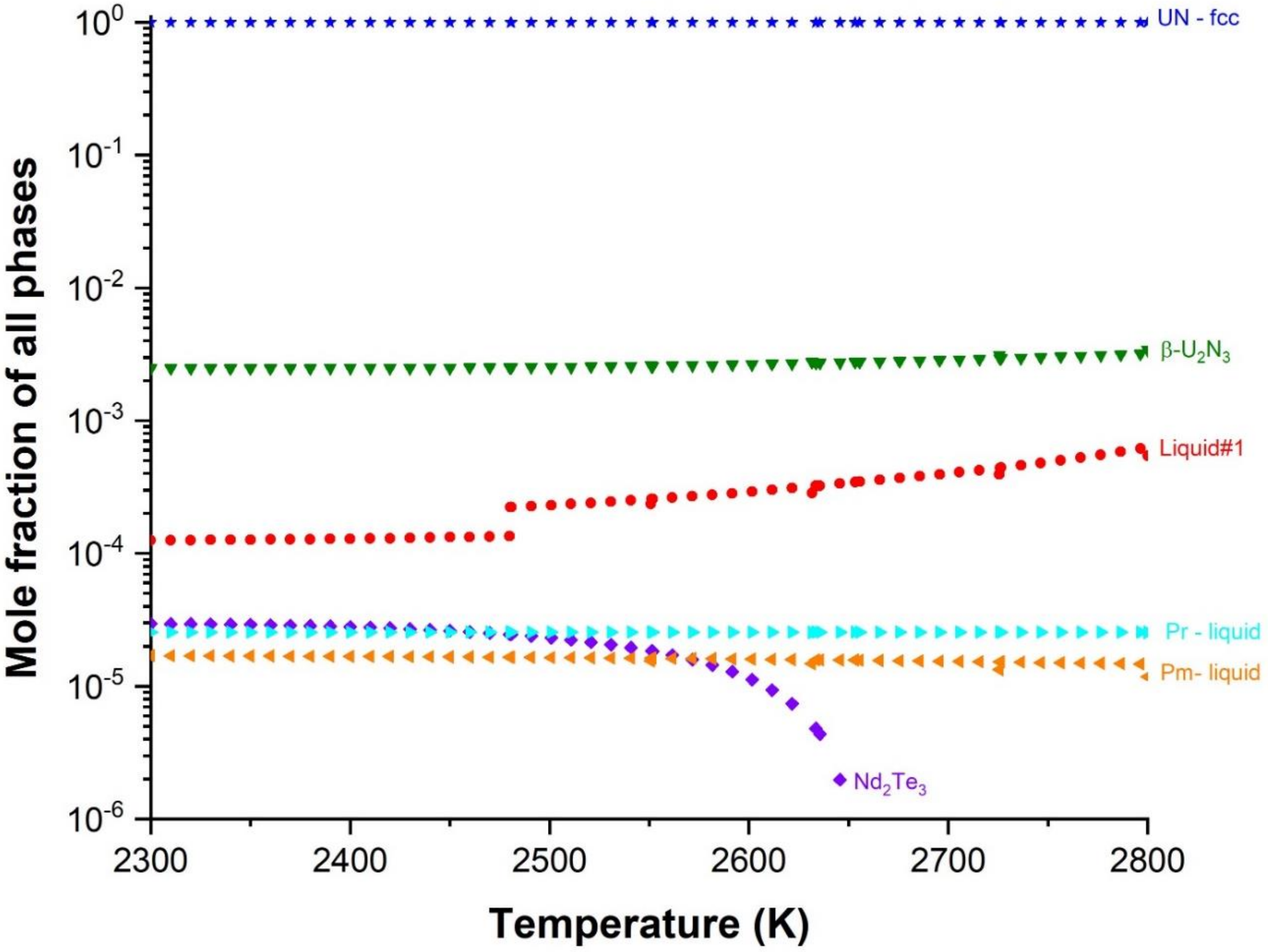
CALPHAD – Computer Coupling of Phase Diagrams and Thermochemistry method
Thermo-Calc 2021b code using SUB3 (SGTE Substances Database v3.3) and TAF-ID (TAF-9) Thermodynamic of Advanced Fuels International database from Nuclear Energy Agency.

Calculation input considerations of systems based on conceptual fuel design:

- Reactor loaded with 100 kg UN fuel operating at 500 MW for 4 h, 2300 – 2800 K at 100 bar
- U-235 thermal fission yields from table C-3-3. – Handbook of Nuclear Data for Safeguards, International Atomic Energy. International Nuclear Data Committee, INDC(NDS)-0534
- Fission Products: H, He, Br, Kr, Sr, Zr, Nb, Mo, Tc, Ru, Rh, Sn, Sb, Te, I, Xe, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu from 10^{-3} to 10^{-6} mol%

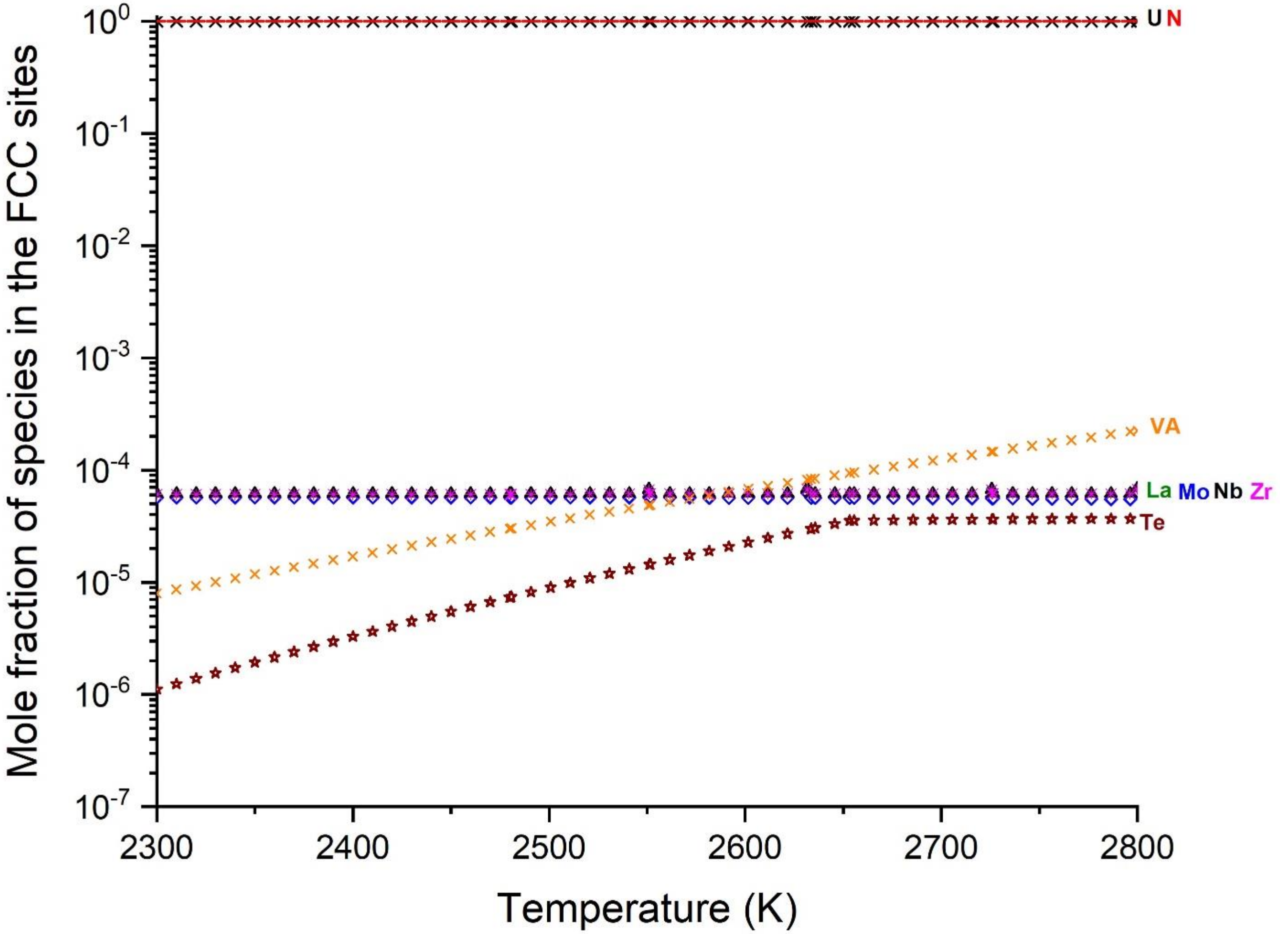
- Calculated products are in thermodynamic equilibrium. Reactions are assumed to not be driven by kinetics.
- Microstructural parameters that affect homogeneity of the components and so the extent of the reactions are not consider here.

Thermochemical calculation – UN



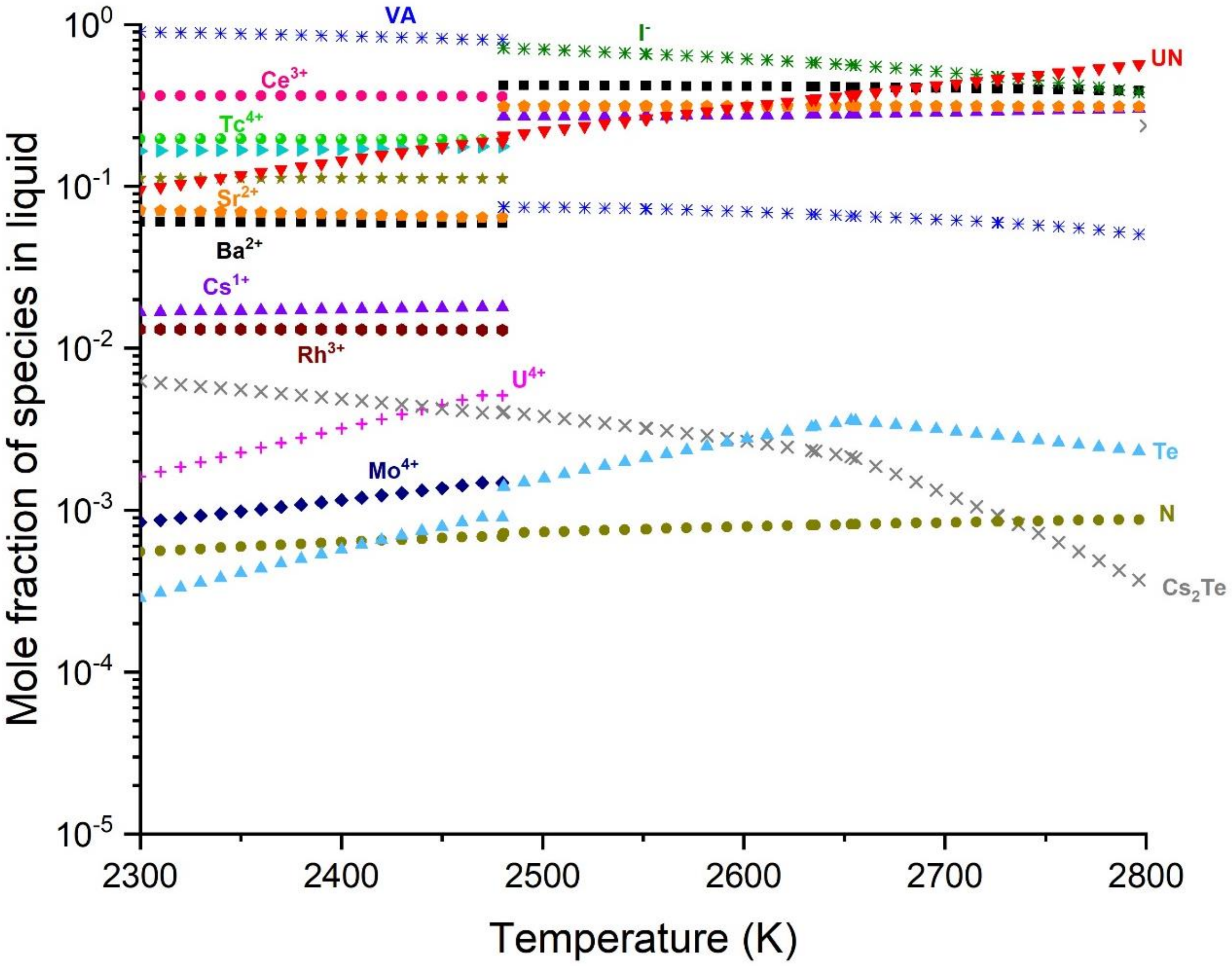
Calculated total amount of phases in equilibrium in the UN fuel at 100 bar.

Thermochemical calculation – UN



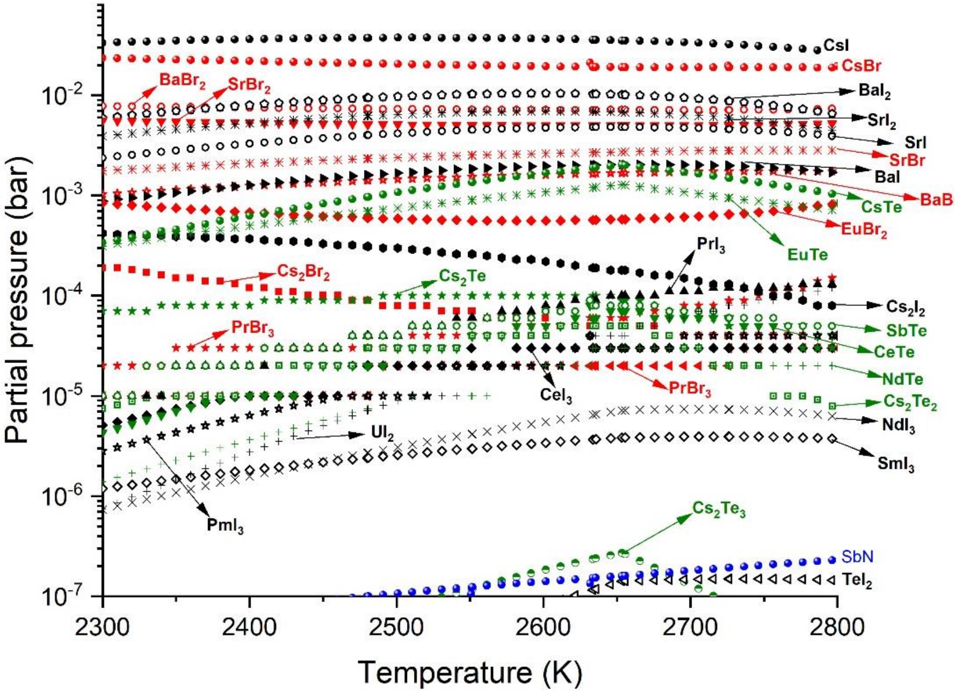
Calculated species site fraction in FCC phase in equilibrium in the UN fuel particle at 100 bar.

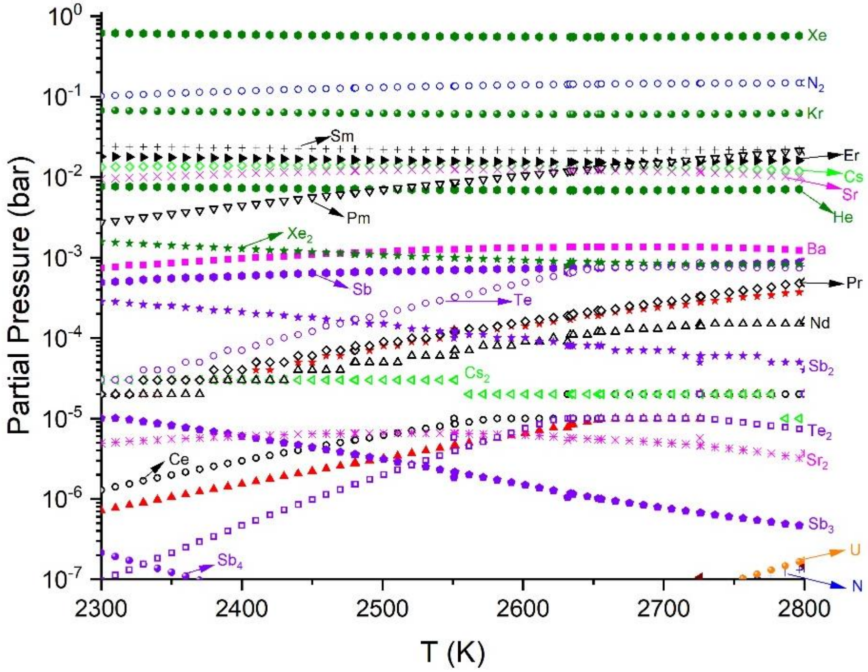
Thermochemical calculation – UN



Calculated species in liquid in equilibrium in the UN fuel particle at 100 bar.

Thermochemical calculation – UN





Calculated amount of vapor species in equilibrium in the UN fuel particle at 100 bar.

General Comments

UN fuel:

- fcc UN, β-U_2N_3 and bcc liquid phases are found to be equilibrium in the fuel during reactor operation from 2300 to 2800 K at 100 bar.
- Fcc UN phase is computed to dissolve low amounts of Mo, Nb, Zr and Te fission products (fps) substituting for U, N and vacancies in the structure.
- Fps Ce, Tc, Sr, Ba, Cs, Rh, Mo and Te are found to be in equilibrium in liquid
- Fps Cs and Te were found to form Cs_2Te in liquid
- The partial pressure of fission products and N2 were calculate to be significant over all reactor operation temperatures.
- Mono and diatomic fps (e.g. Xe, Kr, Sm, Cs, Ba, Sr, He, Xe_2 etc) gas species were computed to form in the gas.
- Halides (e.g. CsI, CsBr, BaI_2, SrI_2) and tellurides (e.g. SbTe, CeTe, NdTe) in the gas

Ceramic Coating Materials

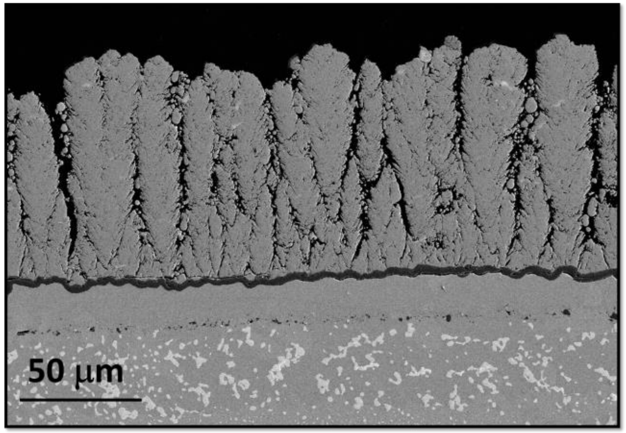
- Thermal Barrier Coatings (TBCs): Reduce heat flux towards the underlying material

7YSZ, 31YSZ, 16RESZ (RE = Y, Gd and Yb), $Gd_2Zr_2O_7$

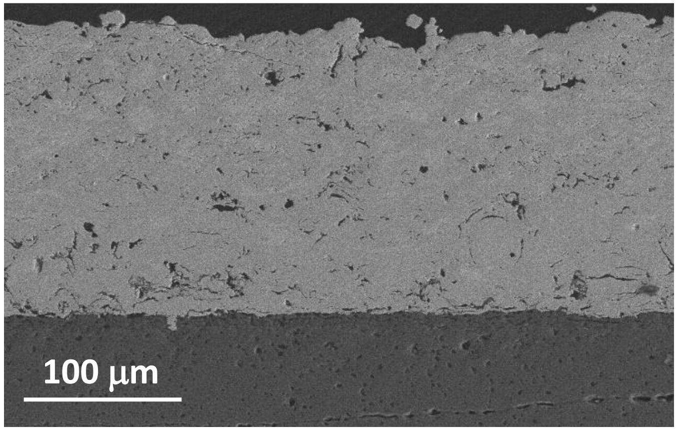
- Environmental Barrier Coatings (EBCs): Barrier to chemically corrosive agents

$Y_2Si_2O_7$ and $Yb_2Si_2O_7$

Thermal Barrier Coating



Environmental Barrier Coating



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

→ ($CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$)

Costa et al, J. Am. Ceram Soc. 2018.

CMAS Corrosion of Thermal/Environmental Barrier Coatings

CMAS + Coating =>Reaction Products

Questions to answer:

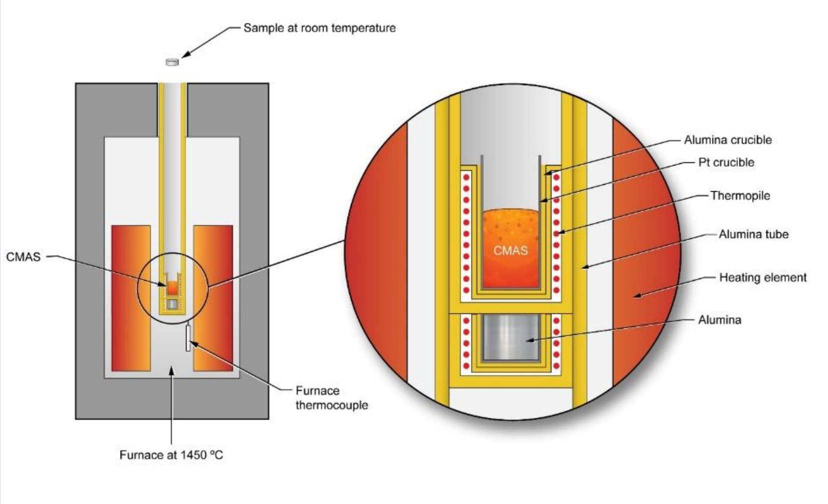
- How reactive is the CMAS with the coating materials?
- Will the coating material react or go into solution?
- What phases will precipitate?
- Is the coating material or the reaction product stable with the CMAS glass?

Questions to be answered with High Temperature Calorimetry

Calorimetric Experimental Techniques

Coating Reactivity with CMAS

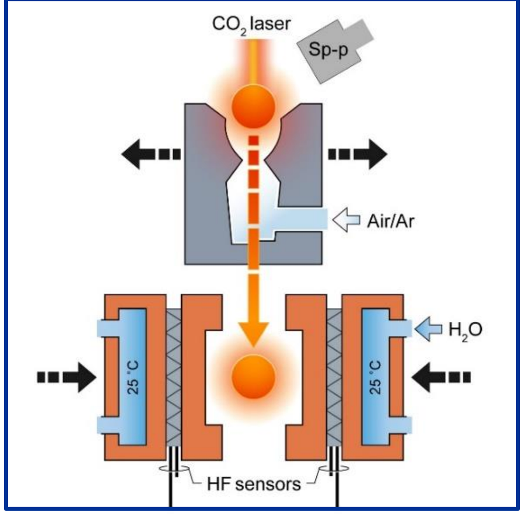
Drop Solution Calorimetry



- Drop in molten CMAS
- Determine enthalpies of solution, mixing and reaction

ΔH_s ΔH_{mix} $\Delta H_{reaction}$

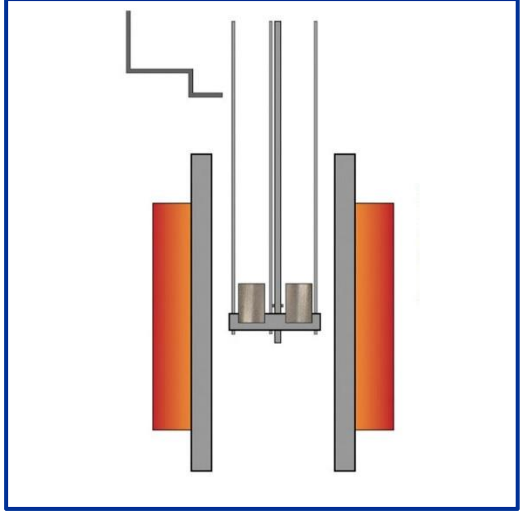
Drop-and-Catch



- Levitated molten coating material
- Determine heat of fusion (>2400°C)

ΔH_{fusion} of 7YSZ

Differential Thermal Analysis



- Measures heat flow during heating/cooling
- Determine heat of fusion (<2400°C)

ΔH_{fusion} of $Yb_2Si_2O_7$ and $CaYb_4Si_3O_{13}$

Combination of these techniques allows for calculation of coating enthalpic reactivity with CMAS

Rare earth Silicates and Zirconia based Coatings and their Binary Oxide components Exposed to Mineral Dust Particles (CMAS) and High Temperature Calorimetry

- Collaboration between NASA GRC and Arizona State University, Davis (Prof. Alexandra Navrotsky)
- Combination of three calorimetric techniques diffraction
- Used molten CMAS as a solvent with varying SiO_2 content

CMAS + Coating => Reaction Products

Coating Materials and their binary oxide components

- TBCs – 7YSZ, 31YSZ, 16RESZ (RE = Y, Gd and Yb), $Gd_2Zr_2O_7$
- EBCs – $Y_2Si_2O_7$ and $Yb_2Si_2O_7$

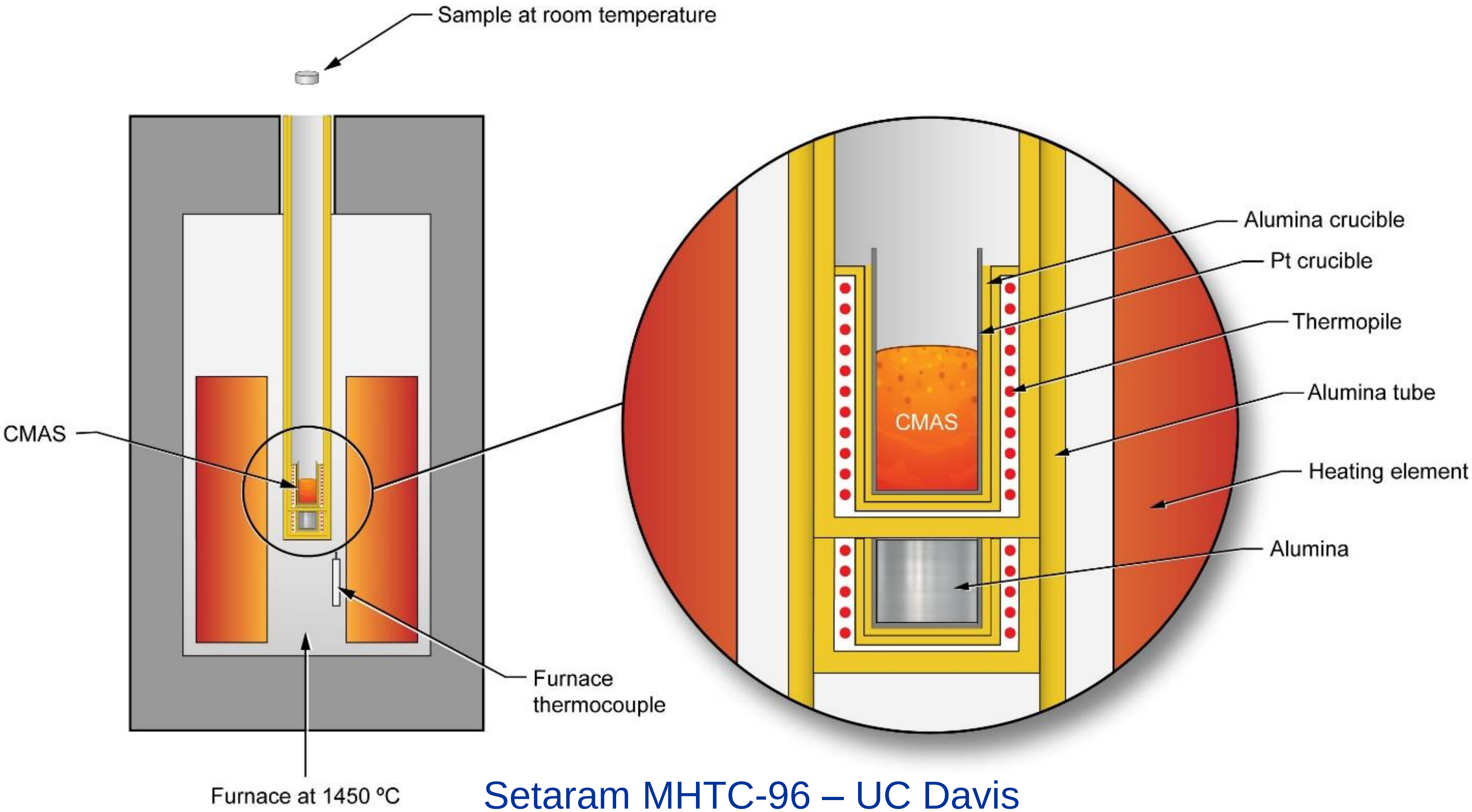
Reaction Products

- Apatites - $CaY_4Si_3O_{13}$ and $CaYb_4Si_3O_{13}$

Costa et al, J. Am. Ceram Soc. 2022.

High Temperature Solution Calorimetry

$$\Delta H_{ds} = \Delta H_{TTD} + \Delta H_{s} \rightarrow \begin{cases} \Delta H_{reaction} \text{ assuming apatite formation} \\ \Delta H_{mix} \text{ knowing } \Delta H_{fusion} \end{cases}$$

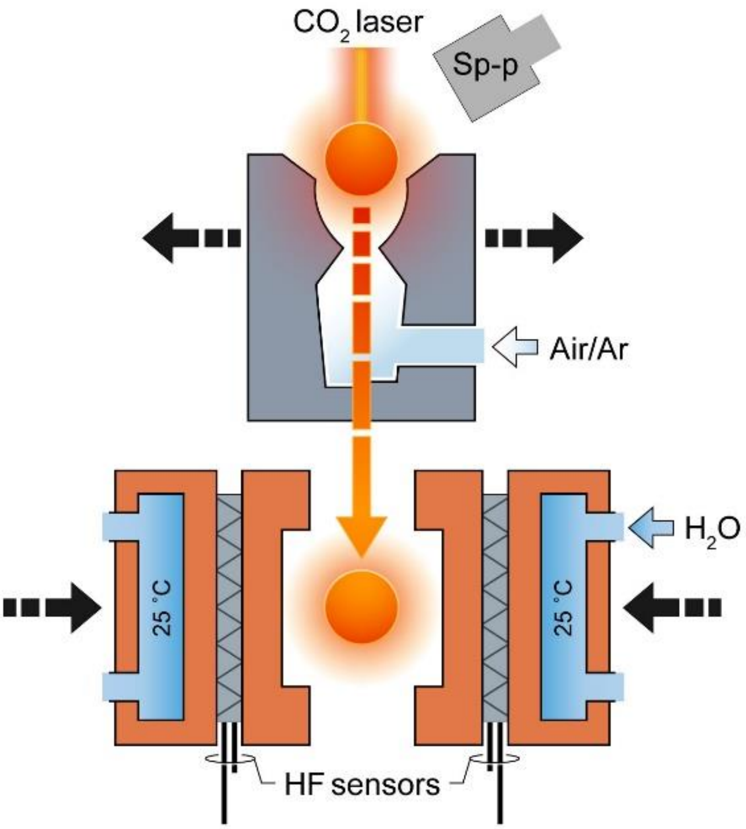


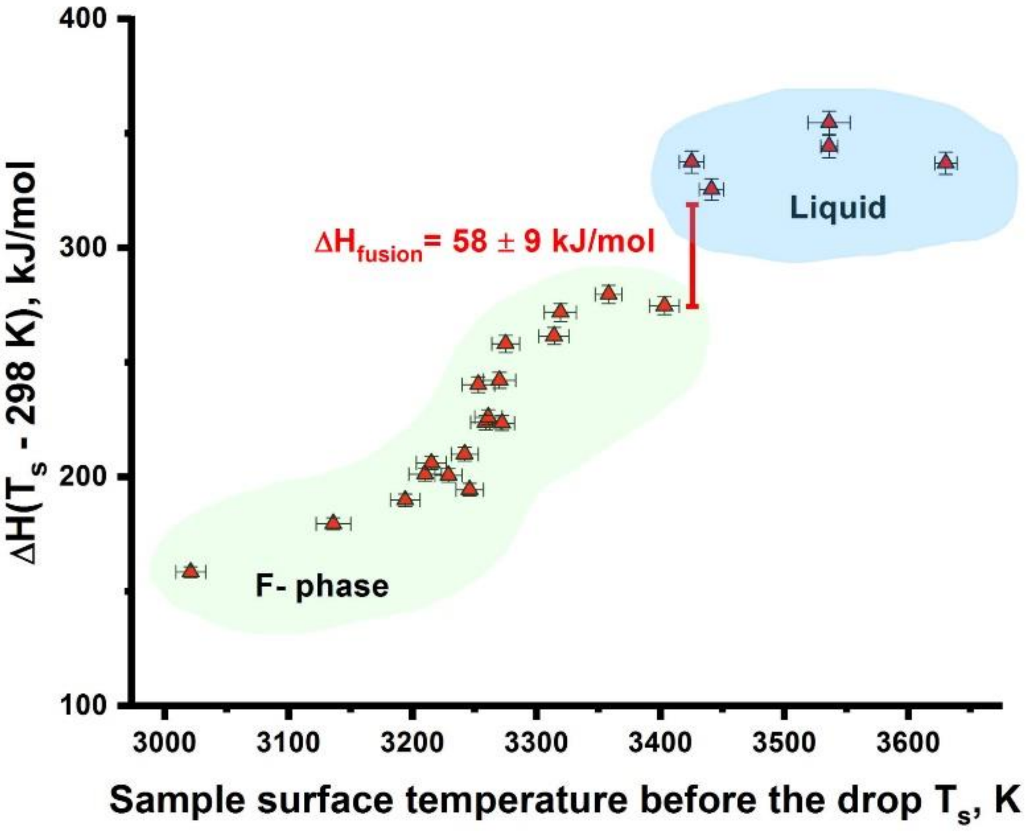
Setaram MHTC-96 – UC Davis

Costa et al, J. Am. Ceram Soc. 2018.

Drop-and-Catch (DnC) Calorimetry

Designed and built at UC Davis





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

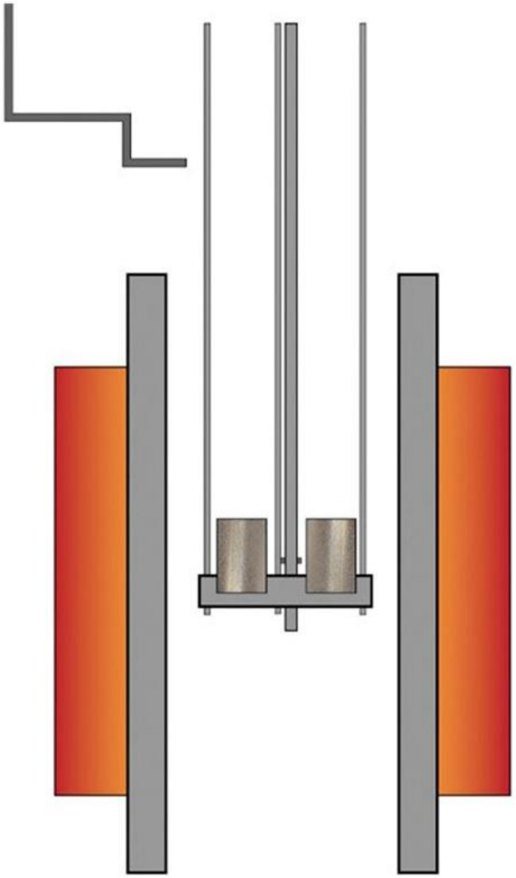
High Temperature Solution Calorimeter

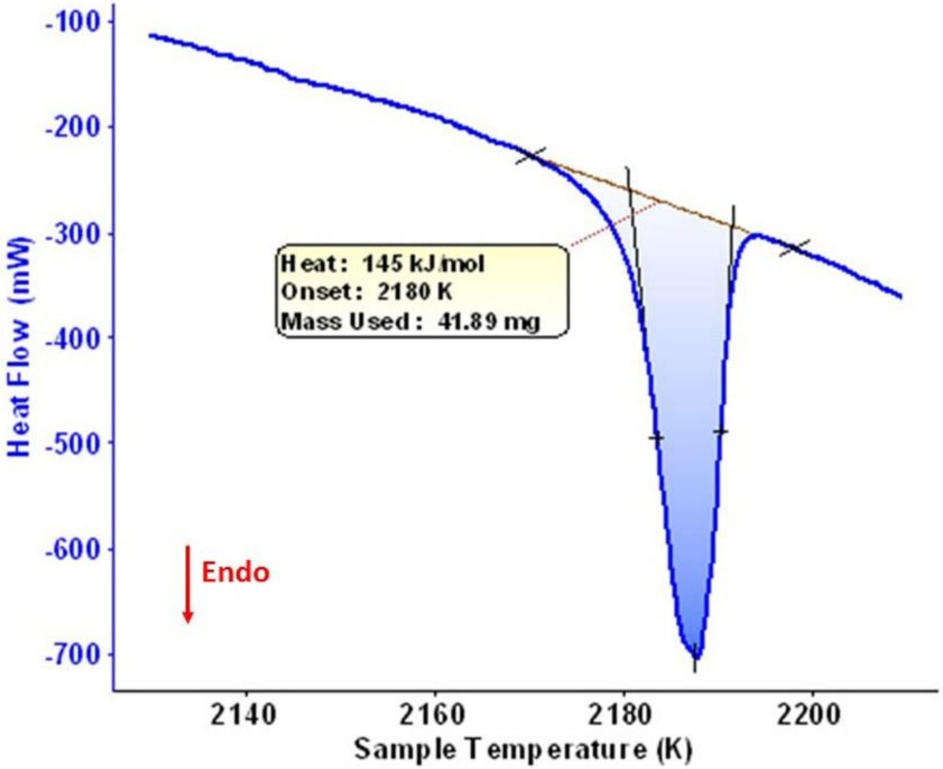
DnC on 7YSZ sample

Costa et al, J. Am. Ceram Soc. 2018.

Differential Thermal Analysis (DTA)

Setaram Setsys Evolution





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

High Temperature Solution Calorimeter

DTA on $Yb_2Si_2O_7$ and $CaYb_4Si_3O_{13}$

Costa et al, J. Am. Ceram Soc. 2018.

CMAS $\mathrm{SiO_2}$ content Effect on Reactivity

- Silicate melts can be envisioned as ionic polymers

- Anionic equilibria*

$Si_2O_7^{6-} = SiO_4^{4-} + SiO_3^{2-}$ **(1)**

$3SiO_3^{2-} = SiO_4^{4-} + Si_2O_5^{2-}$ **(2)**

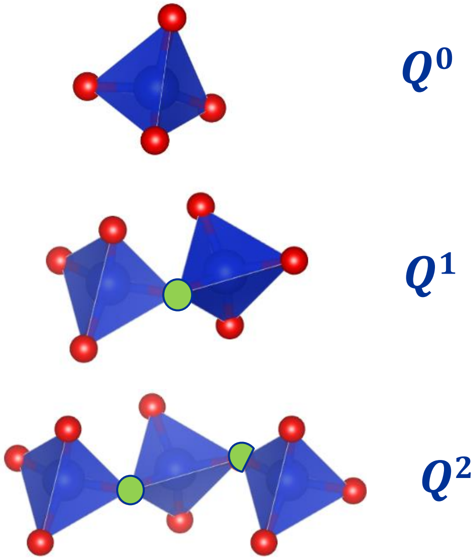
$Si_2O_5^{2-} = SiO_3^{2-} + \mathrm{SiO_2}$ **(3)**

- Q^n notation**

$2Q^3 = Q^2 + Q^4$ (4)

$2Q^2 = Q^1 + Q^3$ **(5)**

$2Q^1 = Q^0 + Q^2$ **(6)**



*****Acid + O^{2-} = Base (7)**

$SiO_3^{2-} + O^{2-} = 2SiO_4^{4-}$ **(8) Slag 35 mol% $\mathrm{SiO_2}$** Q^2

$Si_2O_5^{2-} + O^{2-} = 2SiO_3^{2-}$ **(9) 42-65 mol% $\mathrm{SiO_2}$** $Q^3 - Q^4$

$\Delta H_{\text{s and mix}}$ ⇨ Reaction is more energetic: more exo (negative) or less endo (positive)

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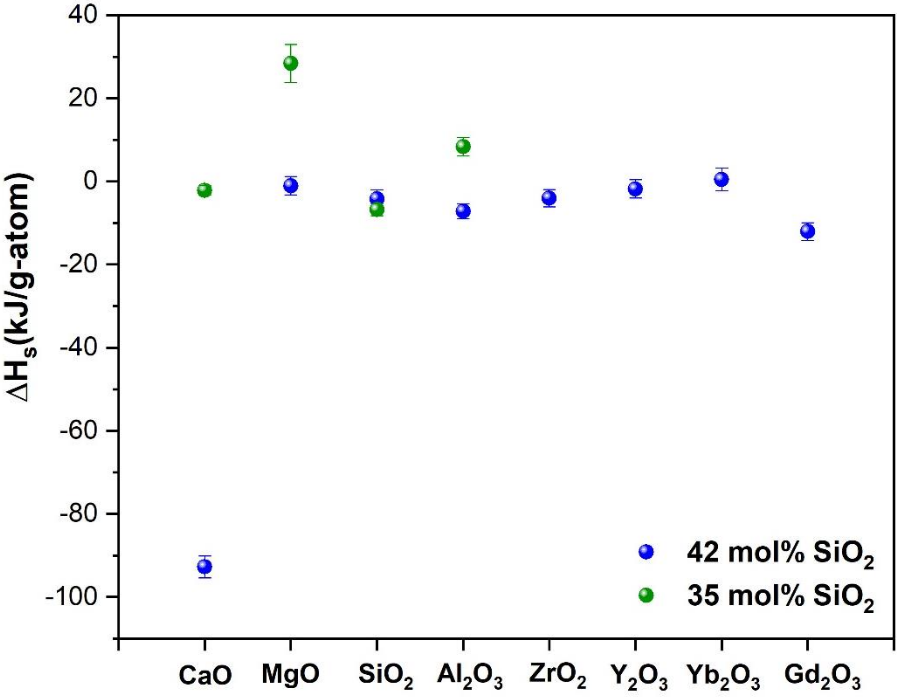
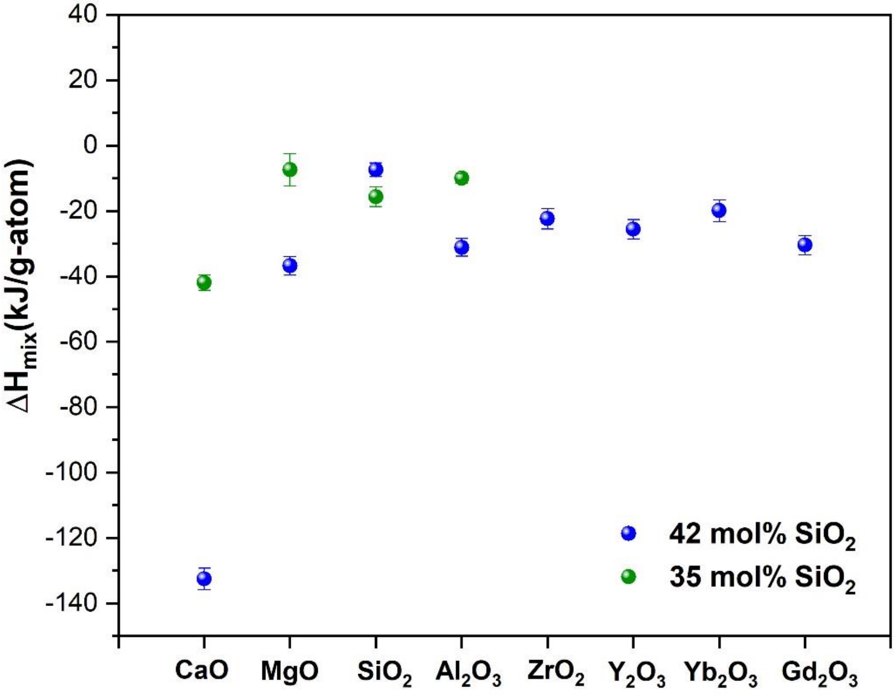
*Virgo et al, Science 1980. **Stebbins, Nature 1987. ***Navrotsky, Rev Miner. 1995.

Calorimetric Results

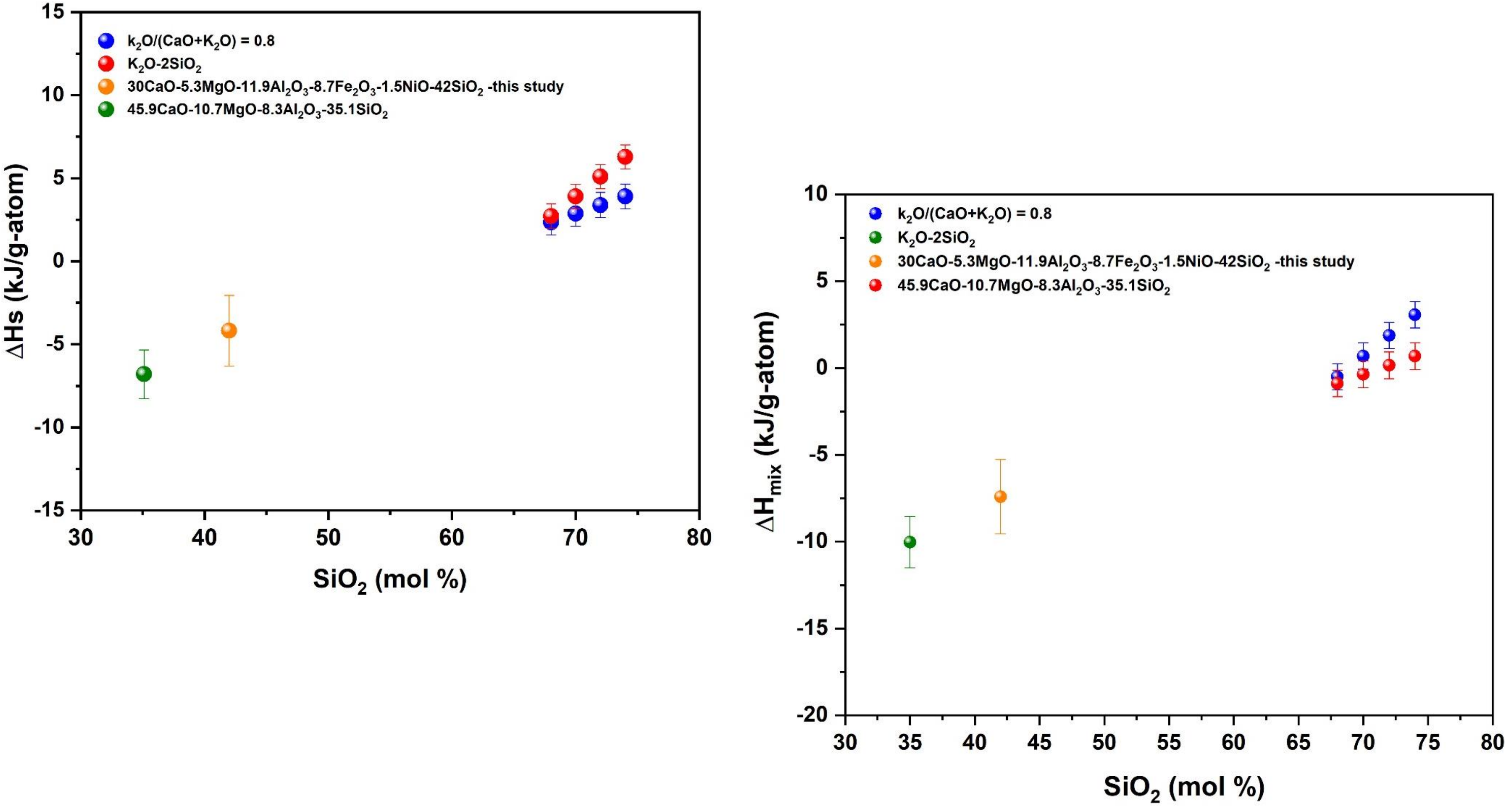




Enthalpies of solution and mixing of binary oxides in CMAS melts with 35 and 42 mole% SiO_2 (green and blue circles, respectively).

Costa et al, J. Am. Ceram Soc. 2022.

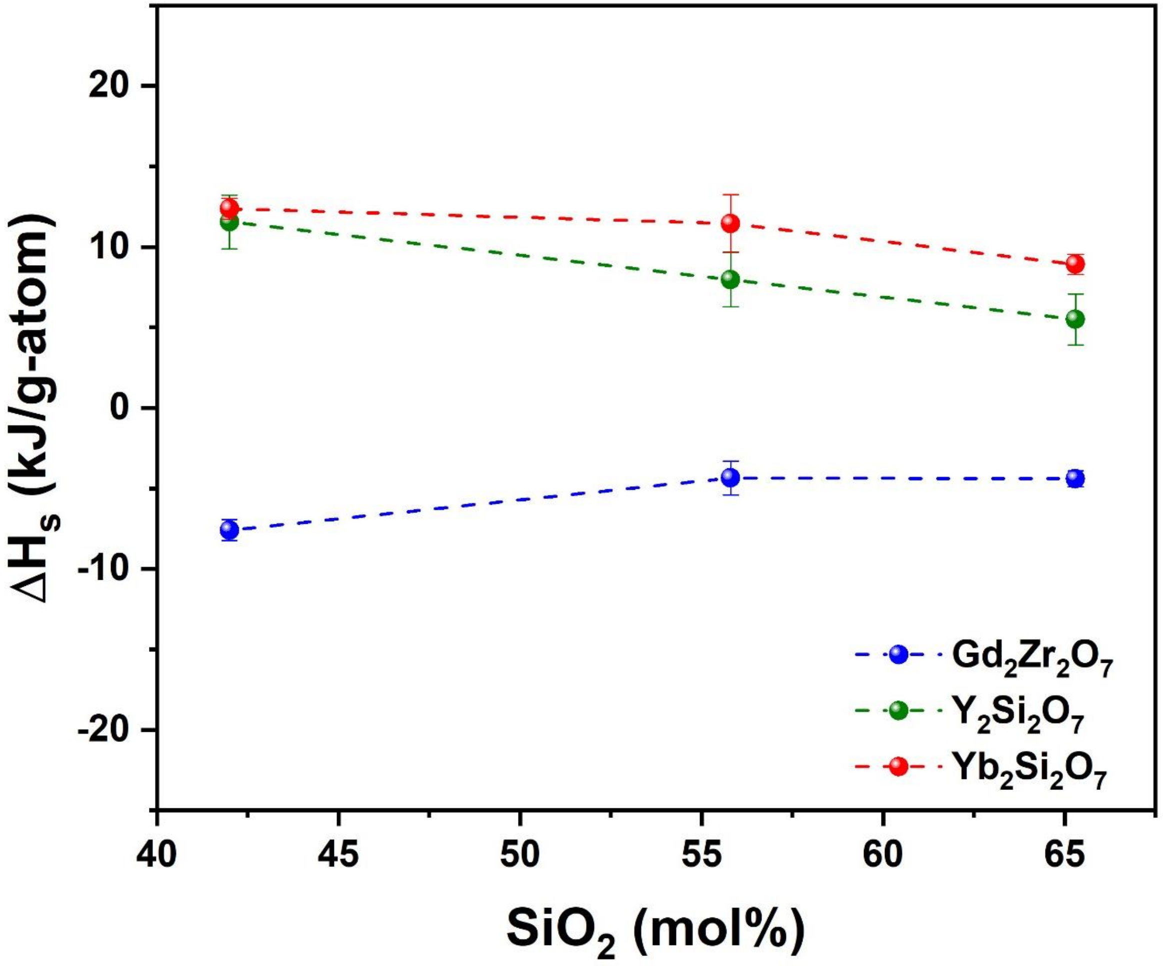
Calorimetric Results



Enthalpies of solution and mixing of SiO$_2$ in silicate melts with varying SiO$_2$ mole percent. Green,21 blue,16and red16 spheres.

Costa et al, J. Am. Ceram Soc. 2022.

Calorimetric Results

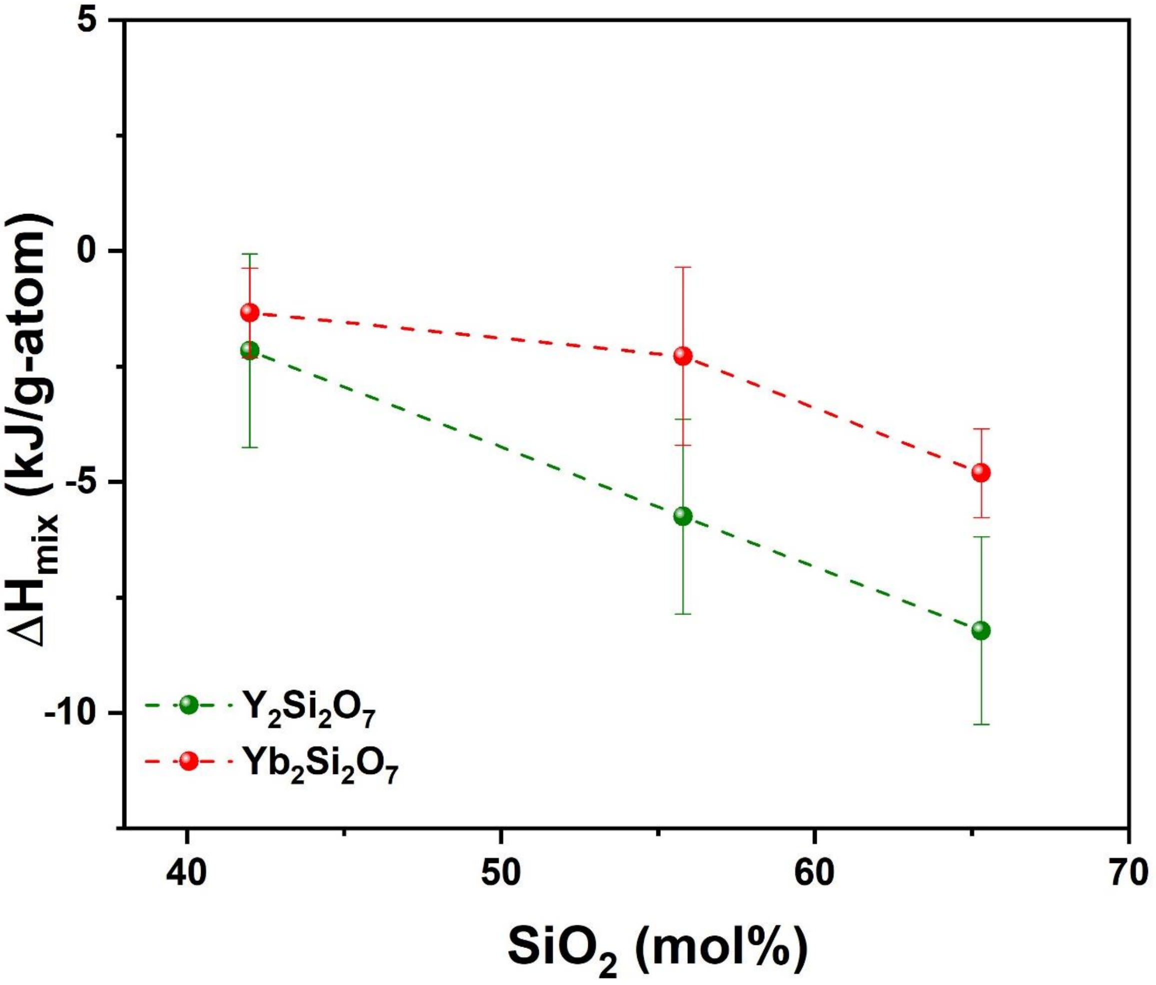


Enthalpies of solution of the $Gd_2Zr_2O_7$, $Y_2Si_2O_7$, and $Yb_2Si_2O_7$ coating materials versus SiO_2 mole percent in CMAS melt.

Increasing SiO_2 content favors reaction for $Y_2Si_2O_7$ and $Yb_2Si_2O_7$ while opposite trend is observed for $Gd_2Zr_2O_7$

Costa et al, J. Am. Ceram Soc. 2022.

Calorimetric Results



Enthalpies of mixing of the $Y_2Si_2O_7$ and $Yb_2Si_2O_7$ coating materials versus SiO_2 mole percent in CMAS melt.

Increasing SiO_2 content favors reaction for $Y_2Si_2O_7$ and $Yb_2Si_2O_7$ while opposite trend is observed for $Gd_2Zr_2O_7$

Costa et al, J. Am. Ceram Soc. 2022.

Calorimetric Results

Material	ΔH$_f$ (kJ/mol)		
	This study, CMAS -1 (42 SiO$_2$ mol%)*	From literature	
			Solvent/method
7YSZ	3.59±3.06	4.77±3.18	Sodium molybdate[**]
31YSZ	1.02±5.86	–6.92±0.70	Sodium molybdate[**]
16RESZ	18.20±3.47	----	----
$Y_2Si_2O_7$	–110.25±14.71	–91.60±4.60	Acid calorimetry, HF[***]
		–112.16	Density Functional Theory, DFT‡
		–67.08±5.98	Alkali borate[†]
$Gd_2Zr_2O_7$	–38.48±9.93	–41.80±1.50	Sodium molybdate[††]
		–52.20±1.50	Sodium molybdate[†††]

*Costa et al, J. Am. Ceram Soc. 2022. **Costa et al Chem Mater. 2010. ***Cordfunke et al, Chem. Thermodyn 1998. ‡Bodenschatz et al, DFT calculated data; 2021.NASA GRC (Unpublished). [†]Fabrichnaya et al, Z Metallkd. 2001.[††]Jafar et al, J Alloys Compd 2021. [†††]Helean et al, MRS Online Proceedings Library 2000.

Summary

- The exothermicity of reaction between coating material or their binary oxide components and the CMAS melt reflects the difference between their acid-base character.
- Enthalpies of solution of YDS and YbDS becomes less endothermic with decreasing SiO_2 mol% while an opposite trend is observed for $Gd_2Zr_2O_7$
- The reactivity of coating materials and their binary oxides with CMAS melts increases with increasing difference in their acid-base character.
- Coating materials formulated from binary oxides with less exothermic enthalpies of solution and mixing are predicted to be less reactive or susceptible to CMAS corrosion.
- The reactivity between the coating materials and the melt is expected to increase with decreasing stability of the coating as a solid or as the coating’s enthalpy of formation becomes less exothermic.

Costa et al, J. Am. Ceram Soc. 2022.