Thermochemical Degradation of $HfSiO_4$ by Molten CMAS

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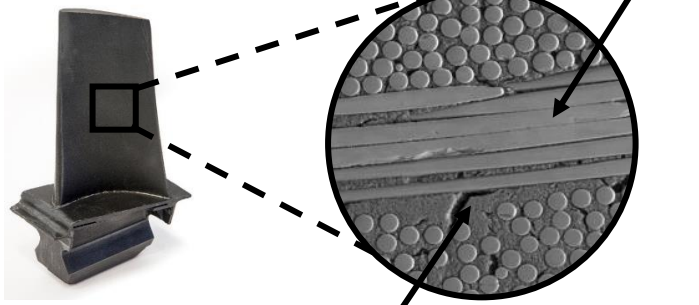
Acknowledgments
NASA Transformational Tools and Technologies Program

Introduction and Motivation – Ceramic Matrix Composites (CMCs)

- CMC turbine engine components offer high temperature stability, but recess in high temperature water vapor environments

GE90 Gas Turbine Engine

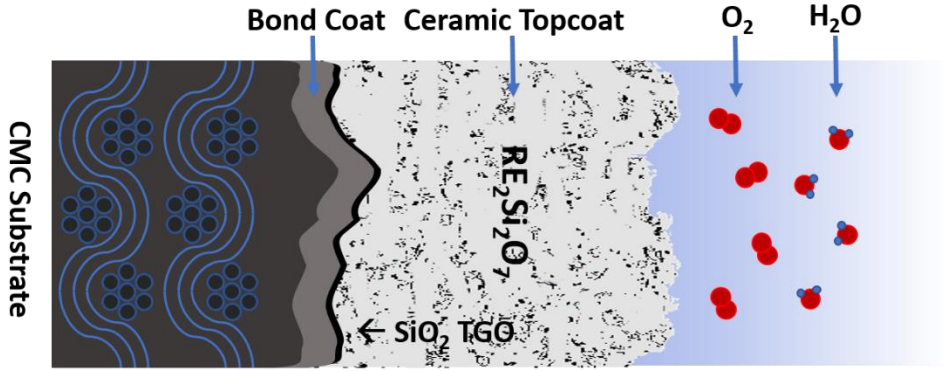


CMC Turbine Blade

$$SiC + \frac{3}{2}O_2(g) \rightarrow SiO_2 + CO(g)$$

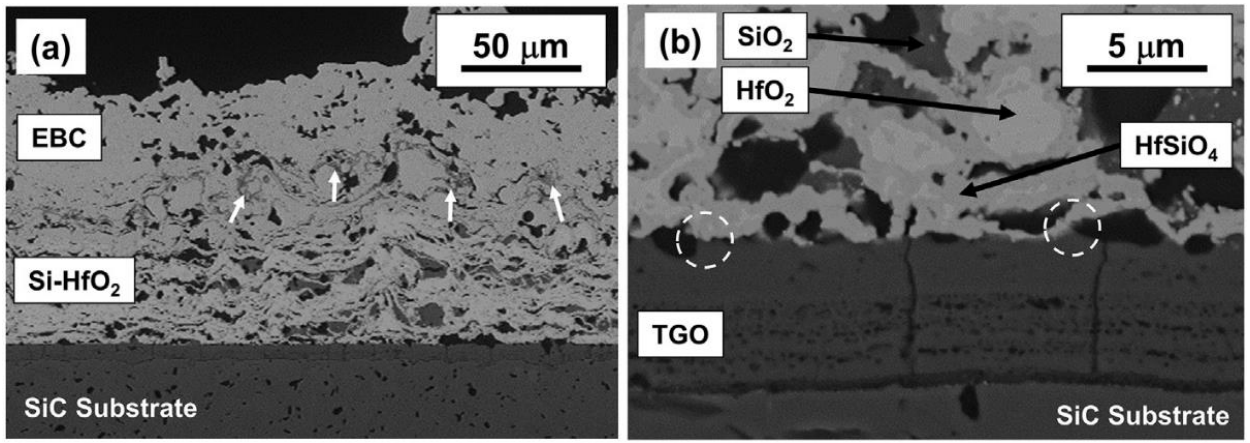
$$SiO_2 + 2H_2O(g) \rightarrow Si(OH)_4(g)$$

Environmental Barrier Coatings (EBCs)

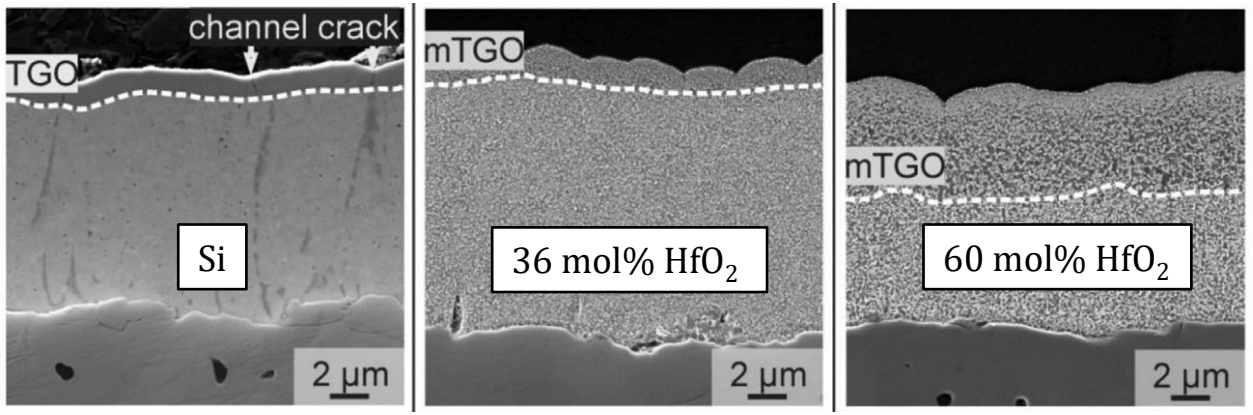


Introduction and Motivation – Bondcoat Development

- Si metal
  - Melting temperature ~1414°C
- HfO_2-Si Composite Bondcoats
  - Higher temperature capability
  - Similar oxidation rate to Si at low HfO_2 content
  - Higher oxidation rate with high HfO_2 content



B.J. Harder, *Surface and Coatings Technology* **384** (2020)



R. Anton et al., *Acta Materialia* **183** (2020)

Introduction and Motivation – Bondcoat Development

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  - Melting temperature ~1414°C
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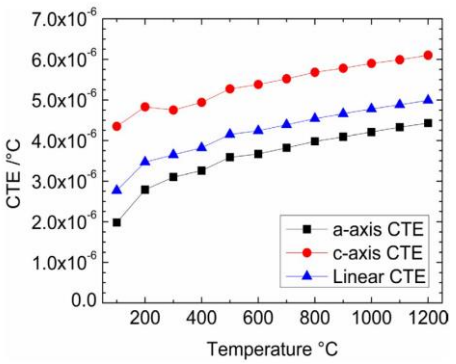
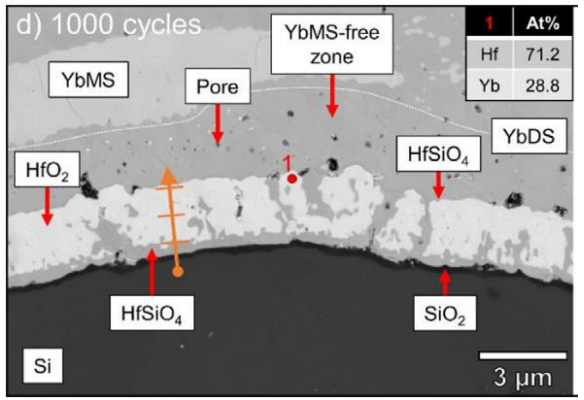
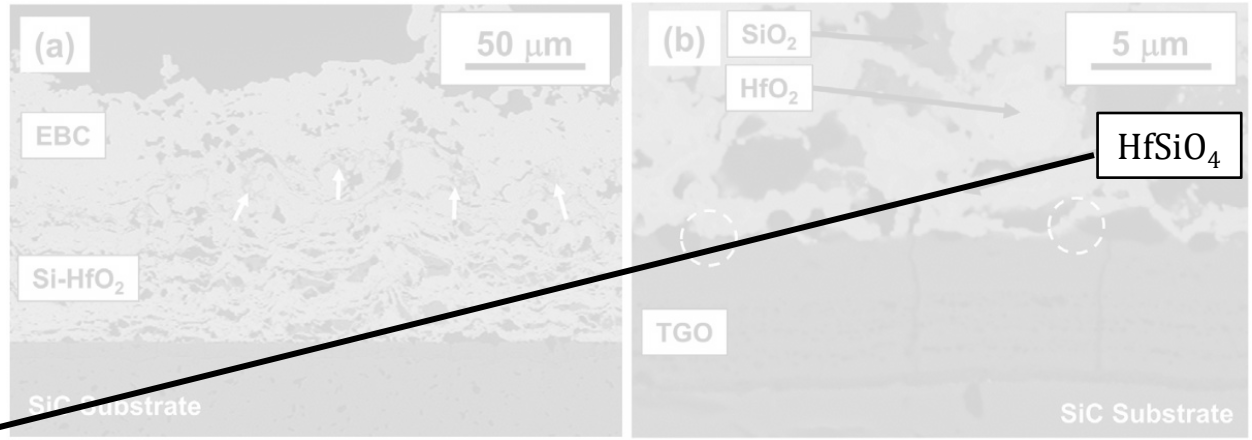
  - Similar oxidation rate to Si at low HfO_2 content
  - Higher oxidation rate with high HfO_2 content
- Hafnon, $HfSiO_4$
  - Reaction product of SiO_2 TGO and HfO_2
  - Similar CTE to Si-based CMCs



Ridley et al., *Journal of the American Ceramic Society* **104** (2021)



Deijkers et al., *Acta Materialia* ***217*** (2021)



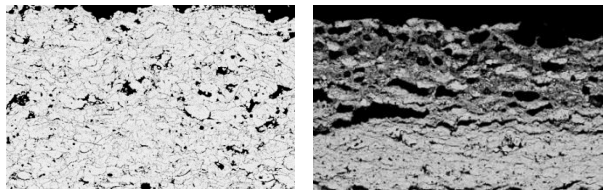
B.J. Harder, *Surface and Coatings Technology* **384** (2020)

R. Anton et al., *Acta Materialia* **183** (2020)

Introduction and Motivation – CMAS Degradation

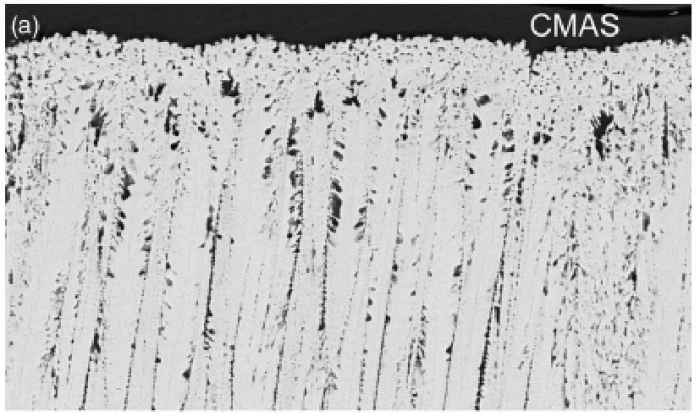
- HfO_2

APS YSZ



Aygun et al., *Acta Materialia* **55** (2007)

EB-PVD YSZ

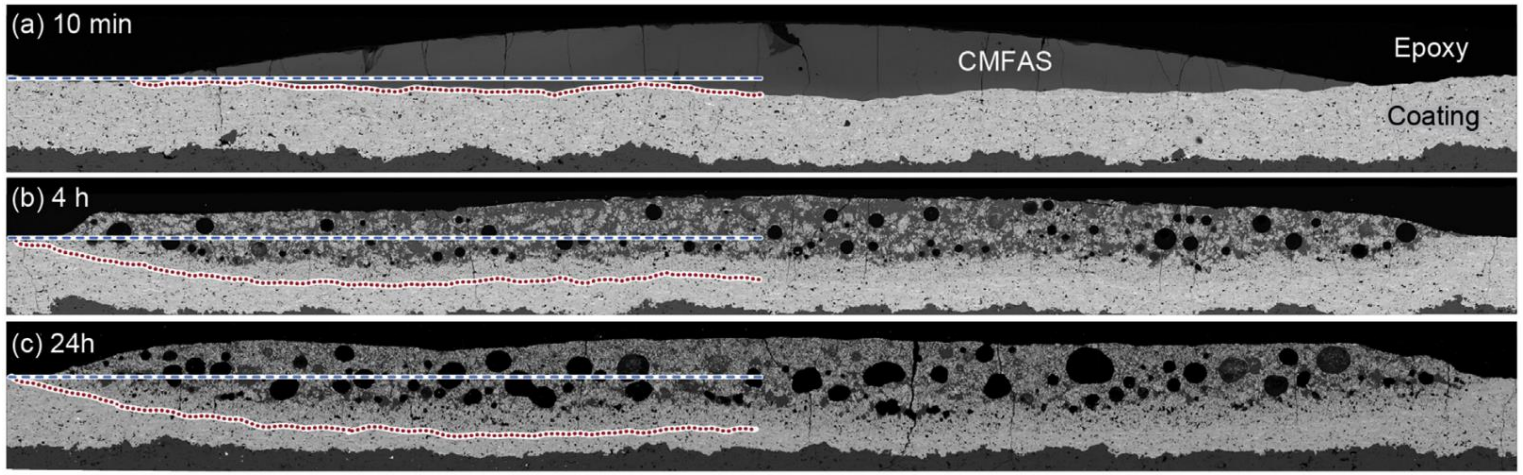


→ m-ZrO_2 + $YO_{1.5}$ leaching into glass

Krämer et al., *Journal of the American Ceramic Society* **89** (2006)

- SiO_2

$4RE_2Si_2O_7 + 2CaO \rightarrow Ca_2RE_8(SiO_4)O_2 + 2SiO_2$

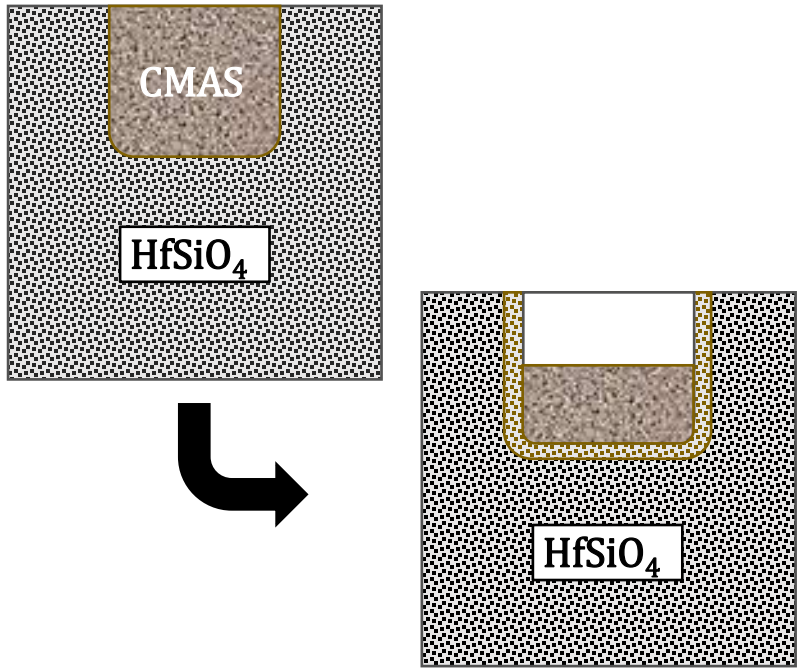


Poerschke et al., *Acta Materialia* **145** (2018)

- HfO_2 – anisotropic CTE, higher CTCE than EBC materials
- Excess SiO_2 results in greater consumption of the coating materials needed to achieve melt saturation

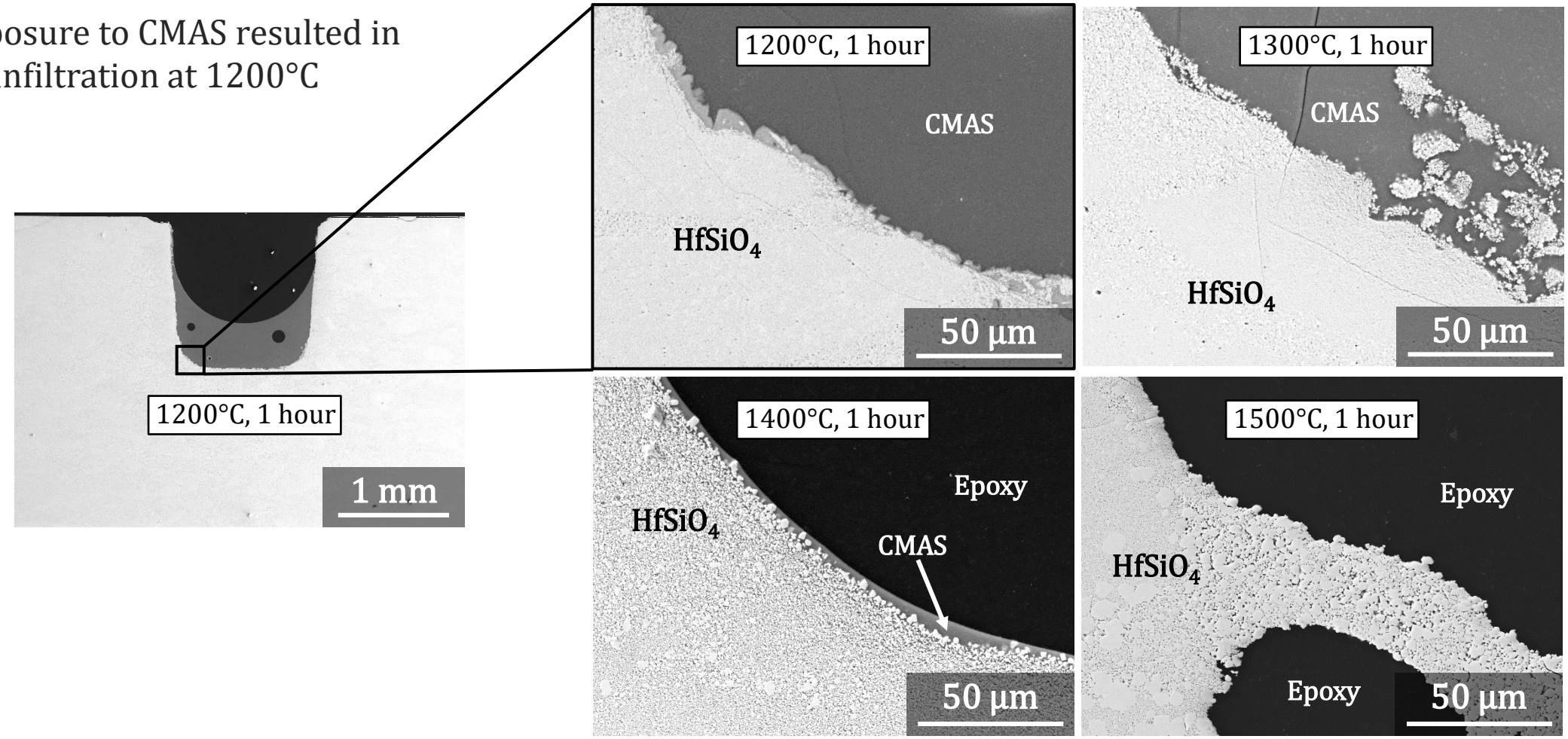
Experimental Procedure and Materials

- Hot pressed $HfSiO_4$
- AFRL-02 CMAS, ~35 mg/cm^2 in drilled wells
  - 34 wt.% quartz (SiO_2), 30 wt.% gypsum ($CaSO_4 \cdot 2H_2O$), 17 wt.% aplite (SiO_2 + $KAlSi_3O_8$), 14 wt.% dolomite ($CaMg(CO_3)_2$), 5 wt.% salt (NaCl)
  - $21.85CaO–6.27MgO–6.08AlO_{1.5}–61.25SiO_2–4.02Na_2O–0.49K_2O–0.04FeO_{1.5}$ (mol.%)
- Samples heat treated at 1200°C, 1300°C, 1400°C, and 1500°C for 1, 10 and 50 hours
- Reaction products and infiltration depth measured using SEM/EDS



Results – CMAS Infiltration

- Exposure to CMAS resulted in no infiltration at 1200°C



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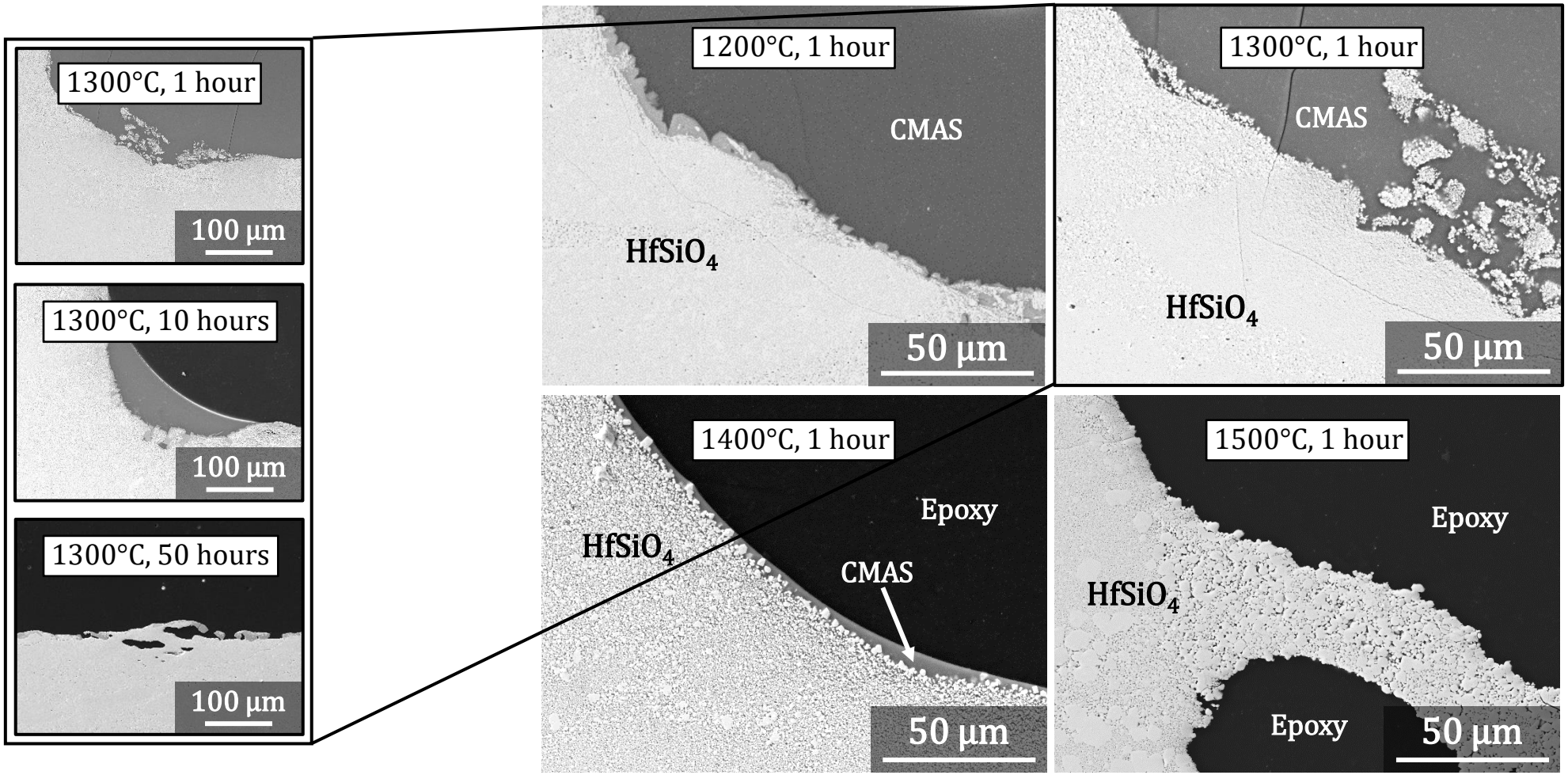

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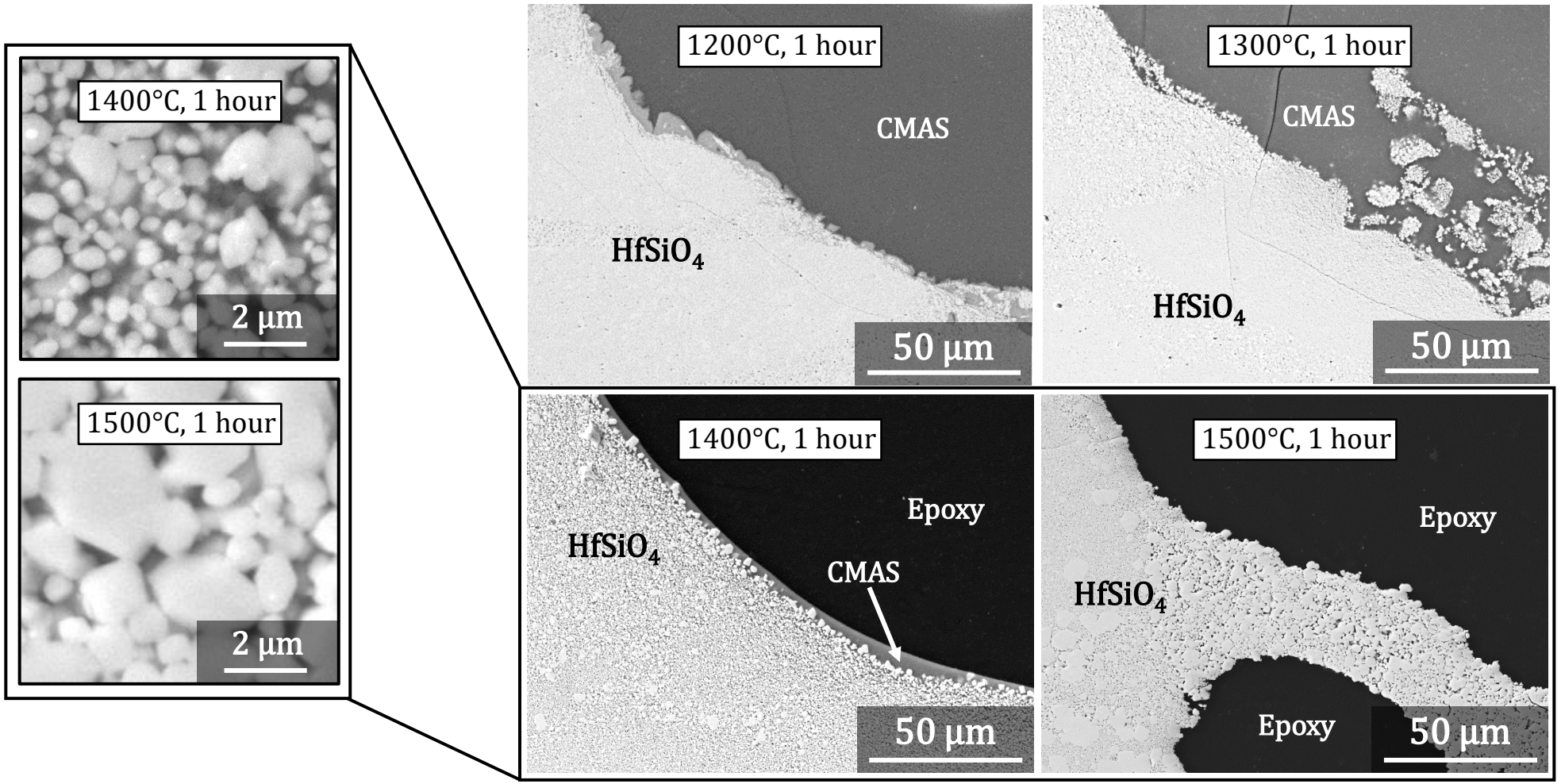
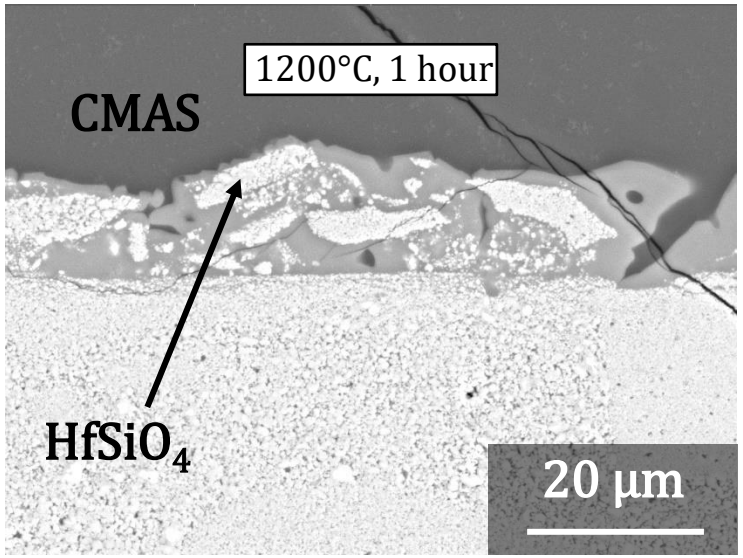
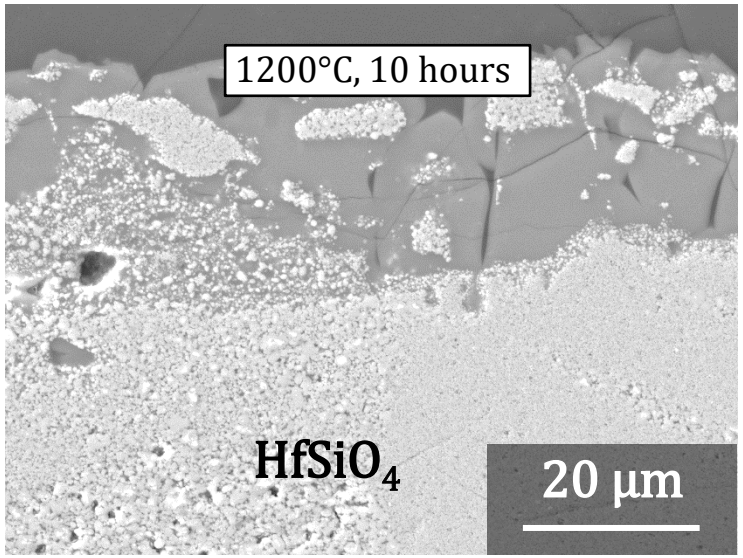
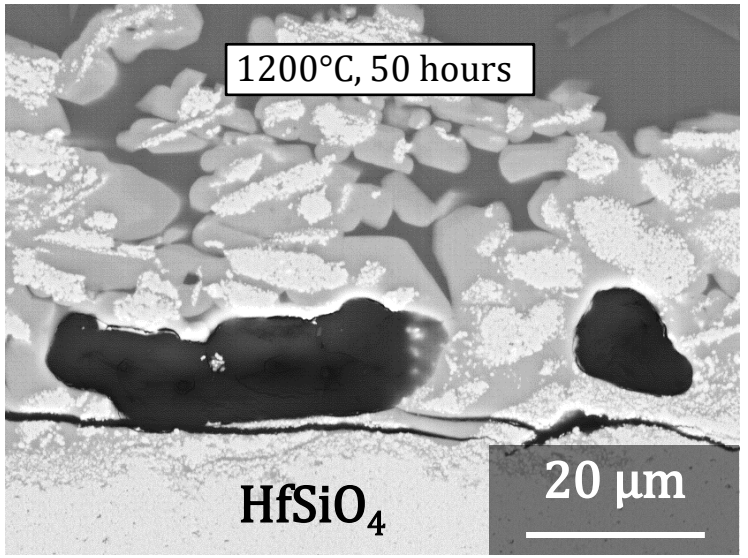


Results – CMAS Interaction Region

- Discontinuous interaction layer former at 1200°C increased in thickness with time
- Clusters of $HfSiO_4$ remain in interaction region







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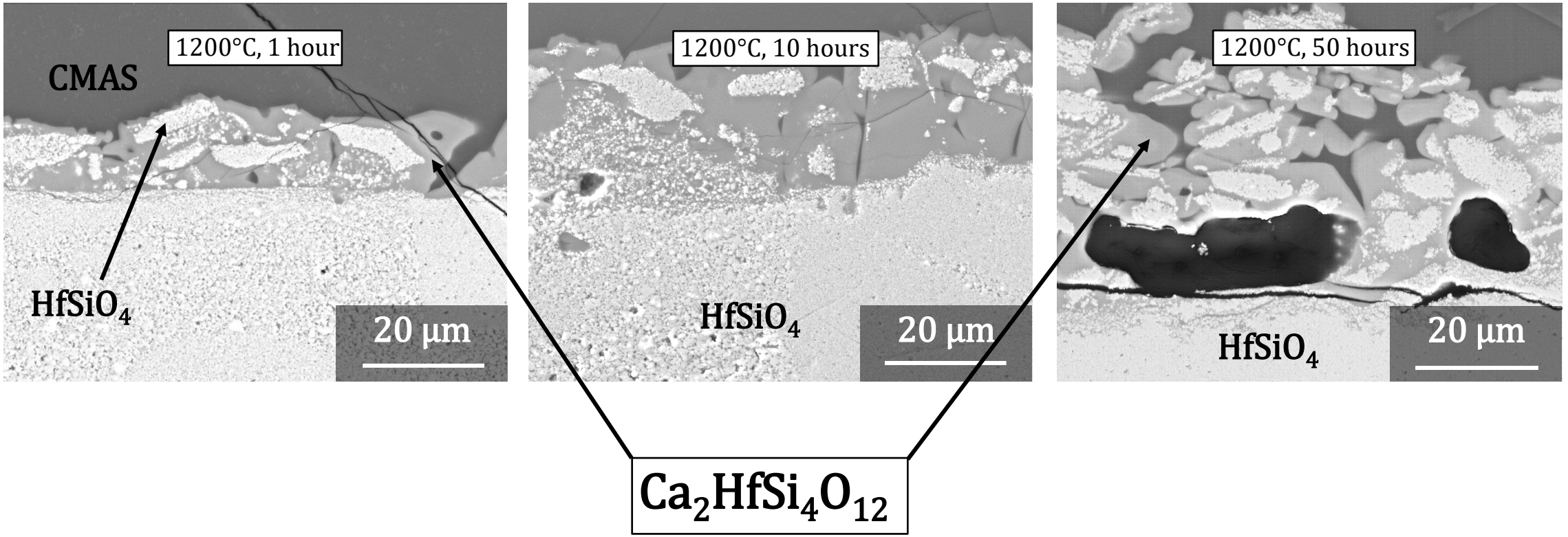

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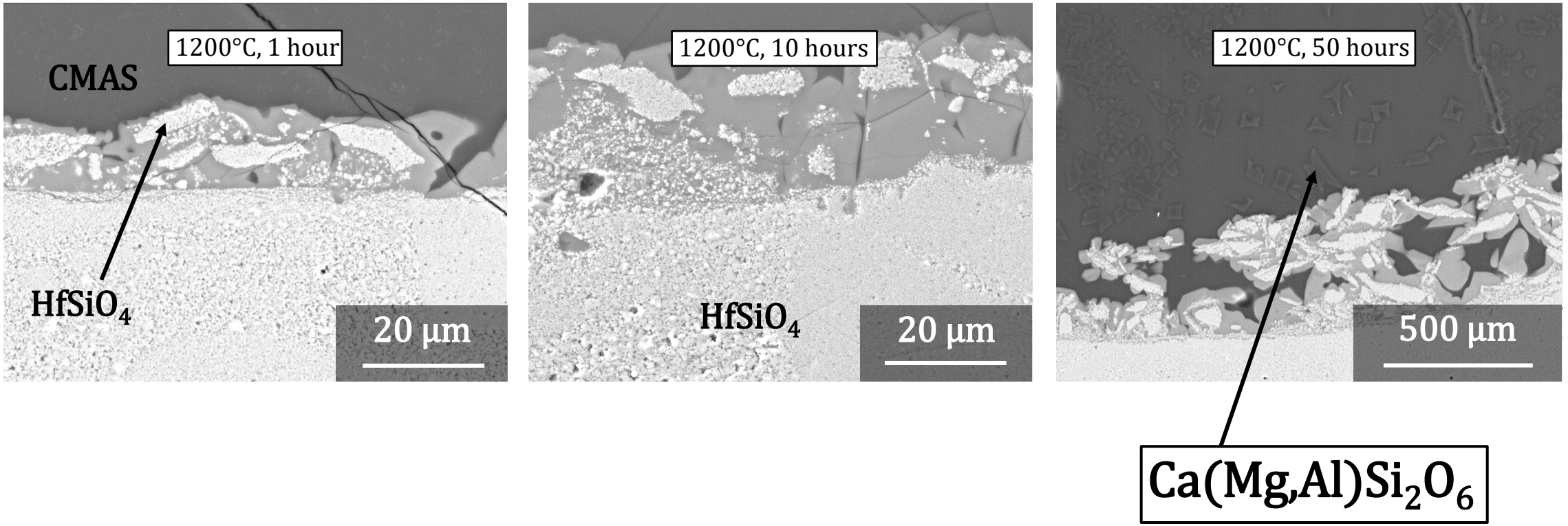
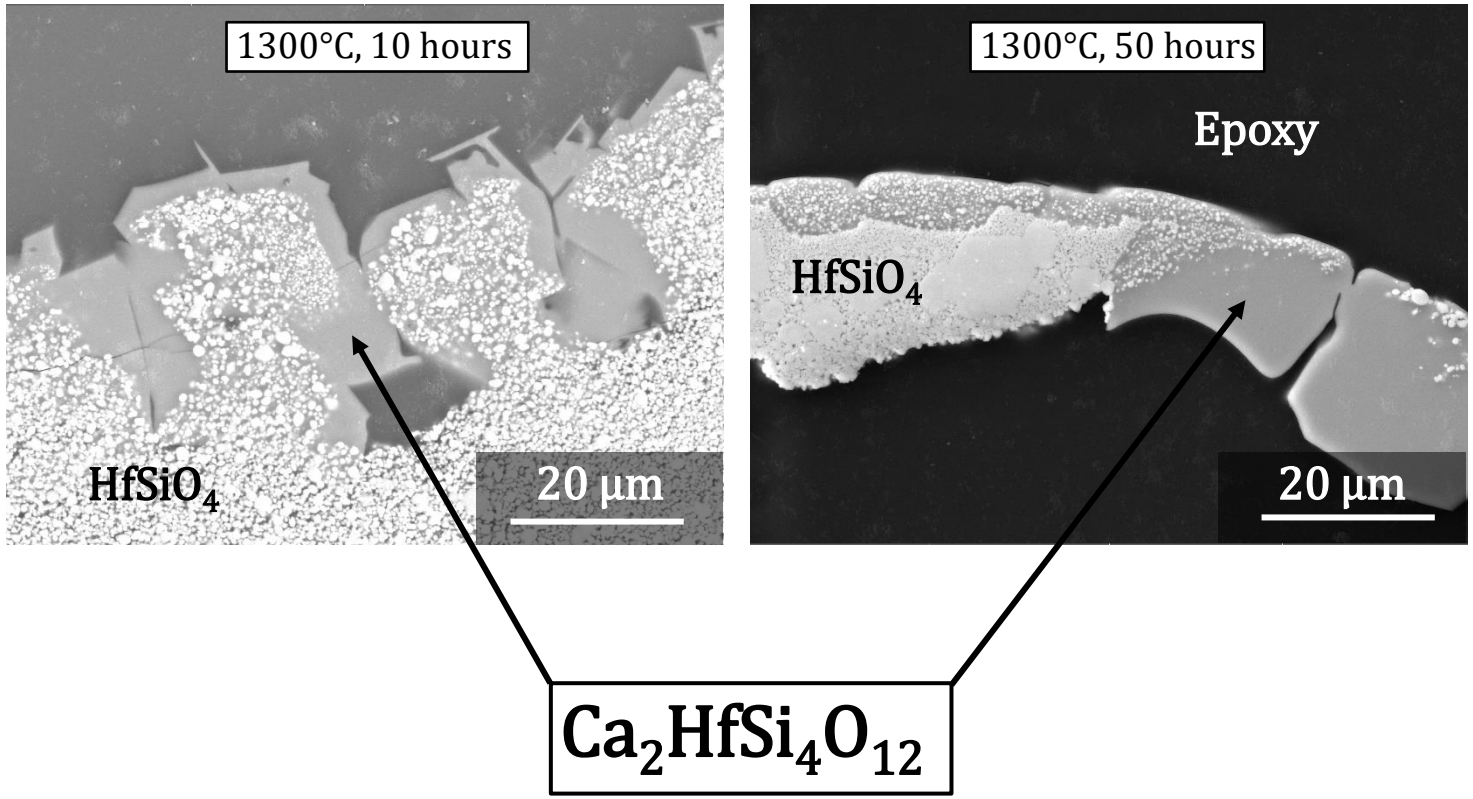


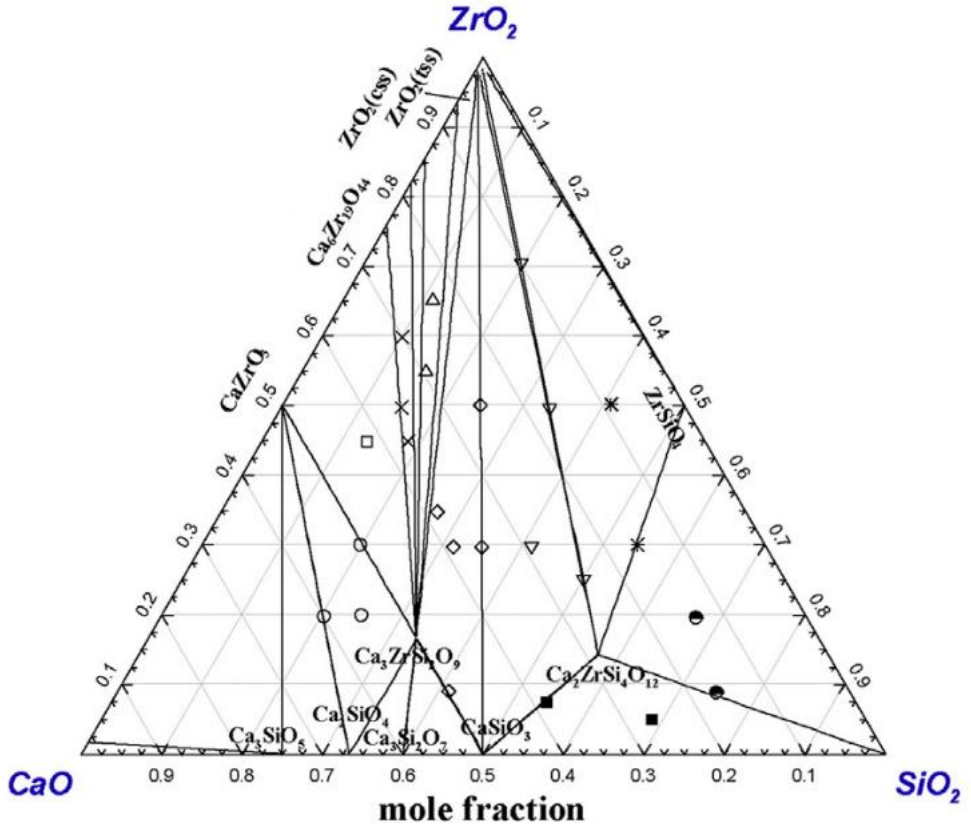
Results – CMAS Interaction Region

- Cyclosilicate phase was observed at longer times at 1300°C but not after 1 hour



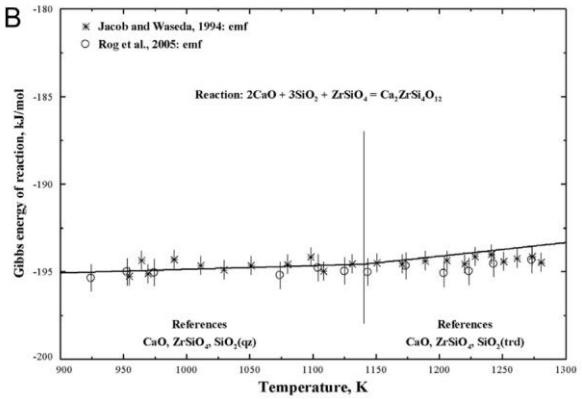
Results – CMAS Interaction Region

- Thermodynamic assessment of CaO-ZrO_2-SiO_2 system at 1300°C

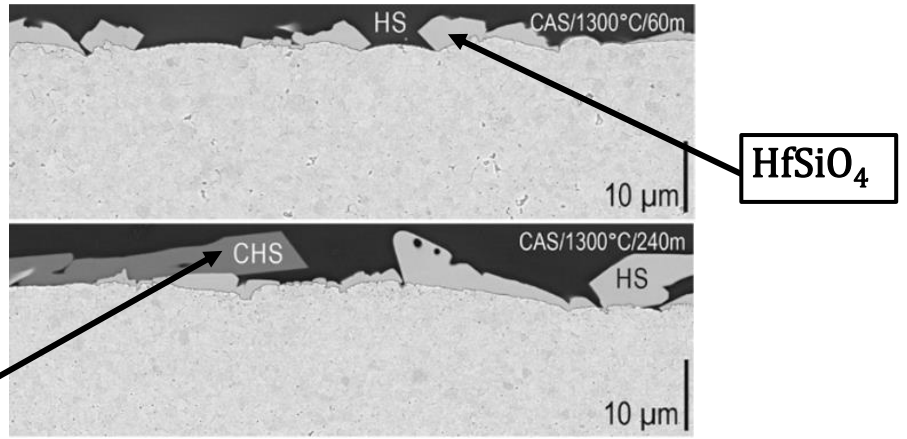


Kwon et al., *Journal of the European Ceramic Society* **37** (2017)

- Gibbs Free Energy Reaction



- CMAS Interaction with HfO_2



Holgate et al., *Journal of the European Ceramic Society* **41** (2021)

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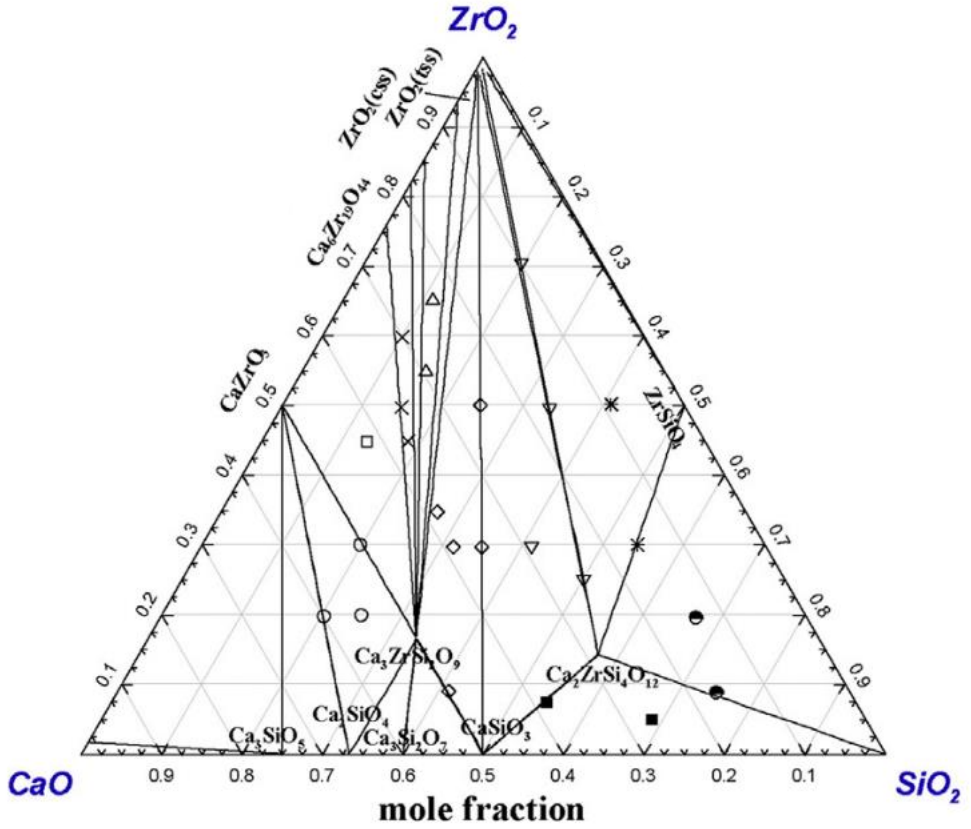

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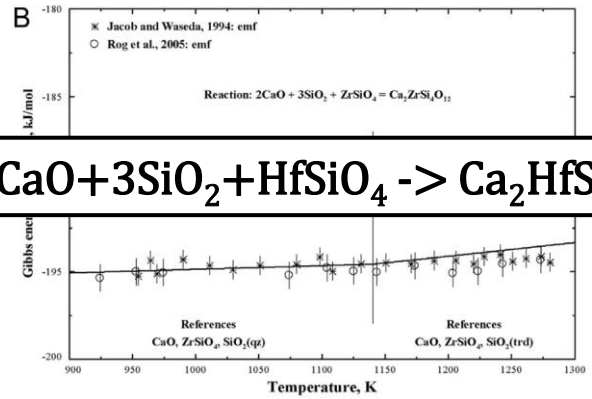
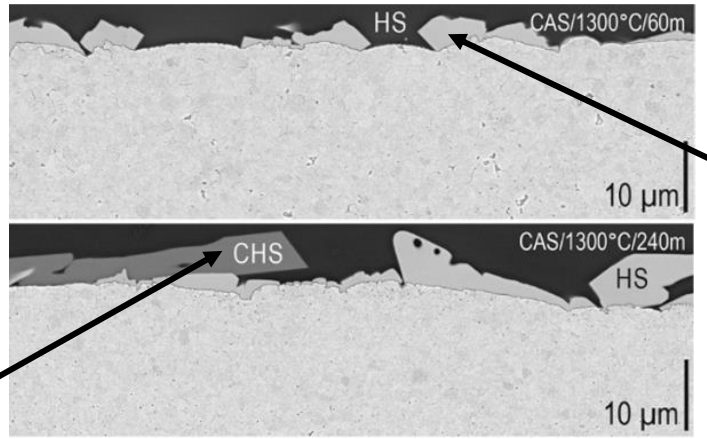


$2CaO+3SiO_2+HfSiO_4 \rightarrow Ca_2HfSi_4O_{12}$

- CMAS Interaction with HfO_2



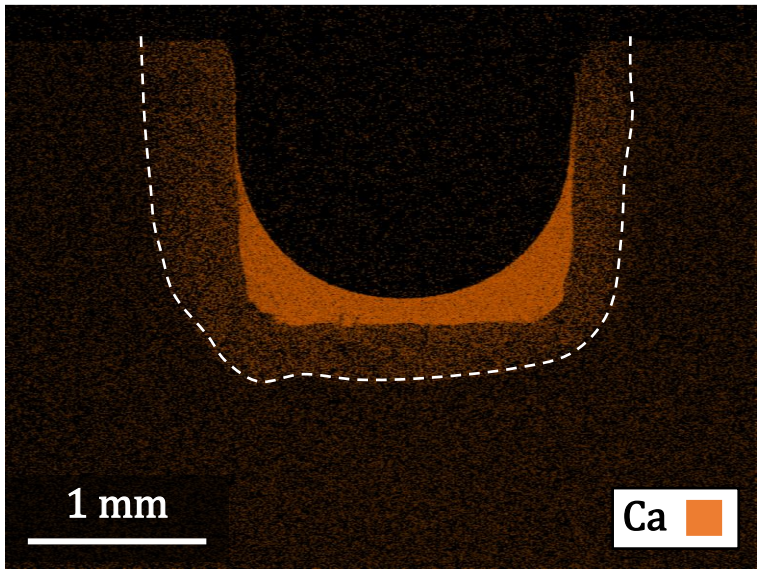
$HfSiO_4$

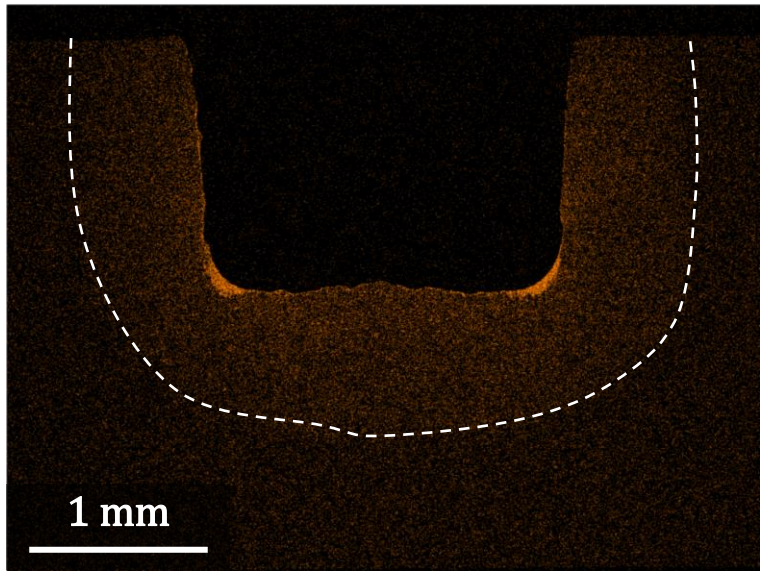
$Ca_2HfSi_4O_{12}$

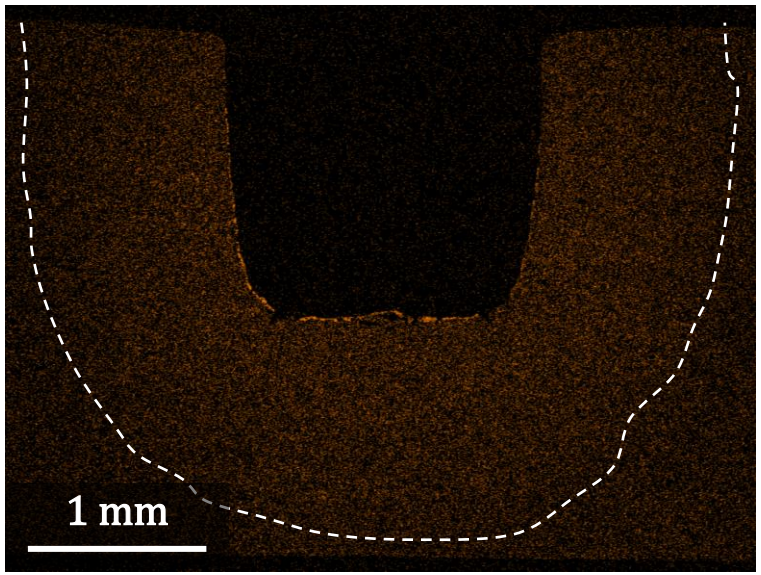
Holgate et al., *Journal of the European Ceramic Society* **41** (2021)

Results – CMAS Interaction Region

- EDS maps of CaO distribution at 1300°C







Results – CMAS Interaction Region

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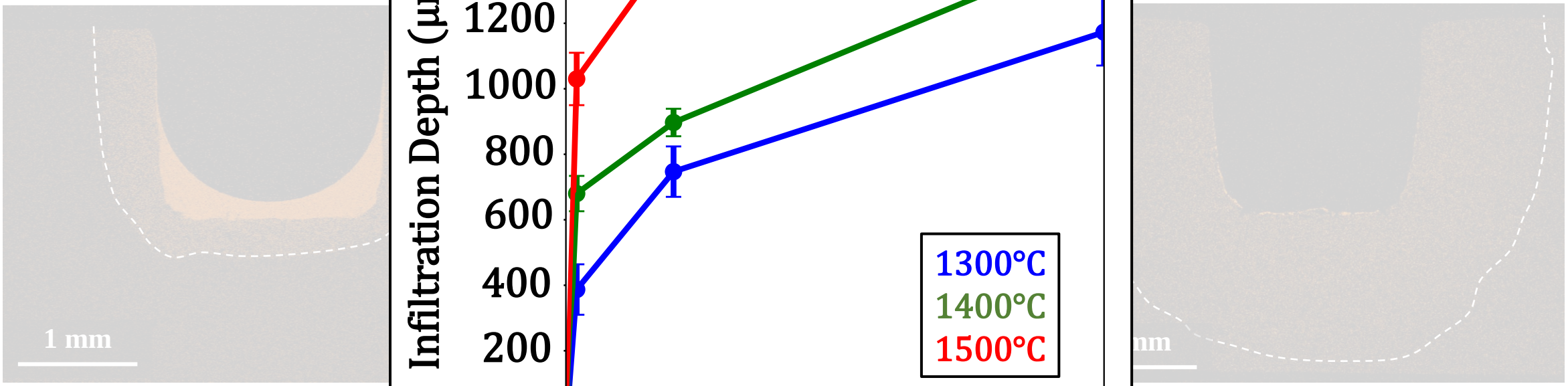
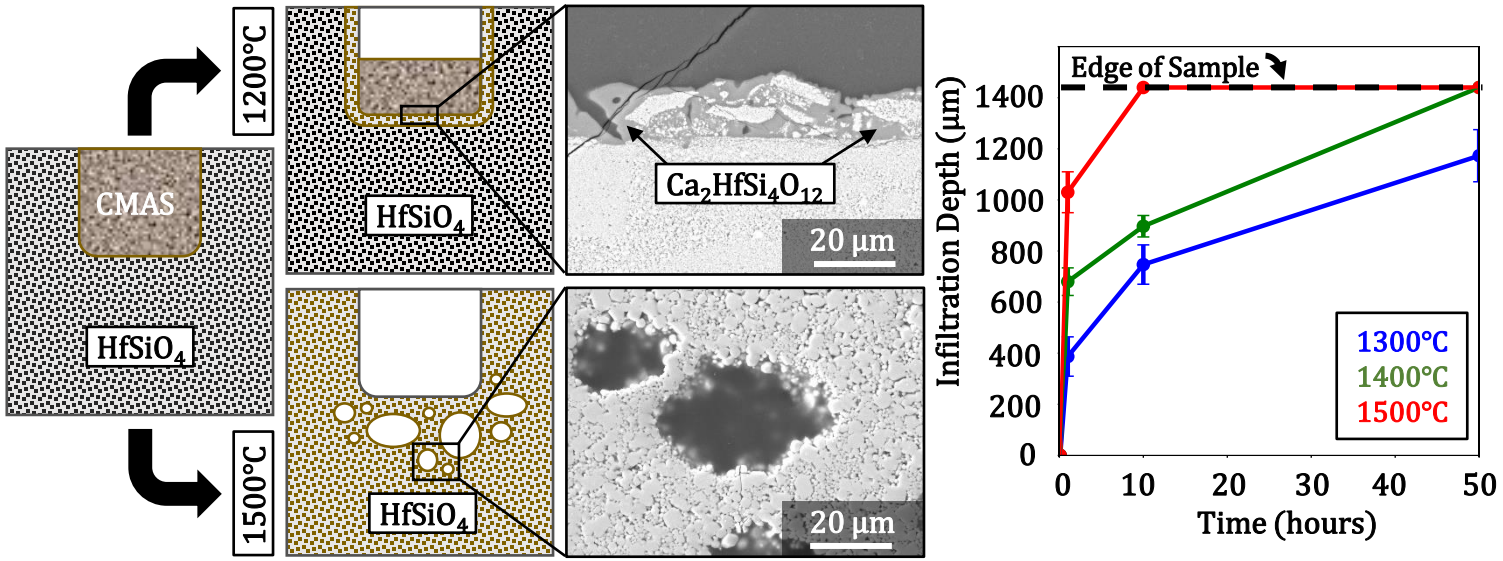


Summary – Thermochemical Degradation of $HfSiO_4$ by Molten CMAS

- Hot pressed $HfSiO_4$ was reacted with CMAS at 1200°C, 1300°C, 1400°C, and 1500°C.
- At temperatures above 1200C, CMAS rapidly infiltrates $HfSiO_4$ through grain boundaries
- A slow growing cyclosilicate ($Ca_2HfSi_4O_{12}$) phase crystallizes at 1200°C and 1300°C, but was not beneficial in halting CMAS ingress



Stokes, J.L., Bansal, N.P., Wiesner, V.L., "Thermochemical Degradation of $HfSiO_4$ by Molten CMAS", *Accepted*, *Ceramics International* (2022)

Thank You!