Crystallization Kinetics of Silica in the Presence of Rare Earth Oxides

PURDUE UNIVERSITY

Materials Engineering

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Rolls-Royce uses environmental barrier coatings (EBC) to protect ceramic matrix composite (CMC) turbine components from volatilization in high temperature combustion environments. Oxidation and subsequent crystallization of the silicon bond layer of the EBC can lead to delamination of the coating. Two experiments investigated how rare earth oxides (REO) found in the rare earth silicate EBC top coat impact the crystallization kinetics of fused silica. Samples with various REO additives were annealed at a range of temperatures and times to construct crystallinity-temperature and crystallinity-time curves. Quantitative X-ray diffraction of annealed samples resulted in varying cristobalite growth rates dependent on the REO additive. The Y_2O_3/Yb_2O_3 blend had the greatest delay of onset crystallization at 1400 °C compared to the SiO_2 (control) at 1300 °C. The time-varying, isothermal data set at 1350 °C loosely followed the Avrami model, but the crystal growth mode could not be determined from the fitting parameters.

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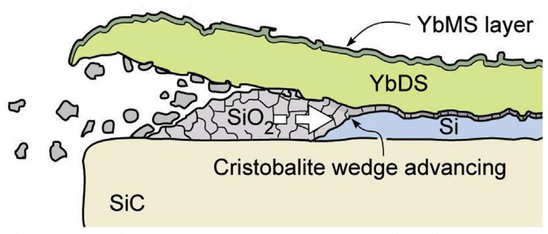
Project Background

Rolls-Royce turbine components use ceramic matrix composites (CMCs) for high-temperature applications. Environmental barrier coatings (EBC) prevent oxidation of the underlying CMC substrate in the combustion environment. The silicon bond coat of the EBC helps adherence of the protective rare earth silicate top coat layer but is susceptible to oxidation at high temperatures. The silica thermally grown oxide (TGO) layer that forms can crystallize and undergo a phase chase, leading to delamination of the EBC.

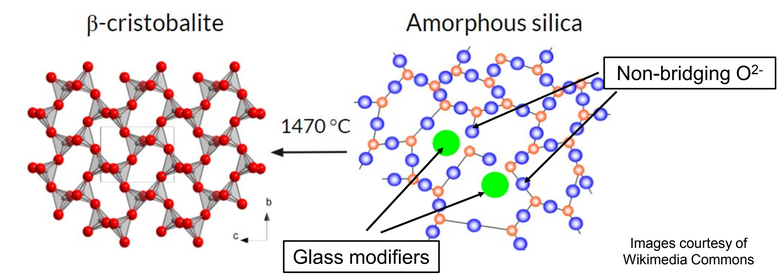


Richards, B.T. et. al. *Acta Materialia* **2016** *106* 1-14

Delaying the onset of crystallization of amorphous silica to its crystalline polymorph cristobalite would improve the lifetime of gas turbine engines. Theory indicates that the diffusion of rare earth oxides (REO) from the outer layer into the thermally grown silica oxide layer promotes crystallization. The project investigates how different REOs affect the crystallization kinetics of silica at high temperatures.

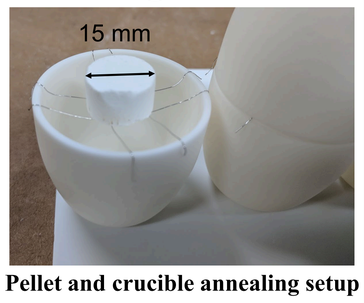
Silica Microstructure

The amorphous structure of fused silica has short-range order characterized by a tetrahedral arrangement of corner O^{2-} ions each shared by two Si^{4+} ions. Rare earth cation impurities may act as glass modifiers, pulling bridging O^{2-} ions out of the network to compensate their charge. Modifiers reduce the number of strong bonds in the glass to lower its viscosity, reducing the energy required to reorder the silica tetrahedron into a crystal lattice.



Experimental Design

All samples were composed of fused silica with 0.5 at% REO additives. Samples were mixed by shaking in a plastic bottle then dry-pressed into ~3.00 g pellets. The powder pellets were annealed in a box furnace using alumina crucibles.



Pellet and crucible annealing setup

Experiment 1:
Effect of REOs on crystallization across a large temperature range at constant annealing time

REO samples tested:
- Y_2O_3, Yb_2O_3, Y_2O_3/Yb_2O_3, Al_2O_3, HfO_2, Al_2O_3/Yb_2O_3, Al_2O_3/HfO_2, and SiO_2 (control)

Annealing temperatures:
- 1200°C,1300°C, 1350°C, 1400°C, 1450°C, 1500°C, and 1600°C

Annealing times:
- All samples annealed 1 hour

Experiment 2:
Effect of annealing times and REOs on crystallization

REO samples tested:
- Y_2O_3, Yb_2O_3, and SiO_2 (control)

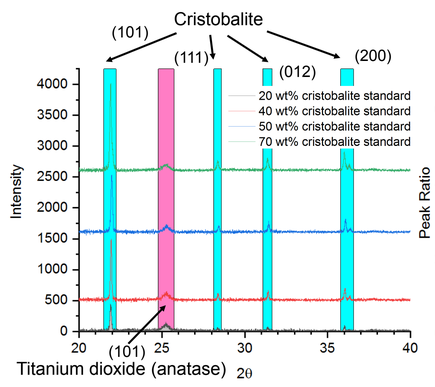
Annealing Temperatures:
- 1250°C, 1300°C, 1350°C,

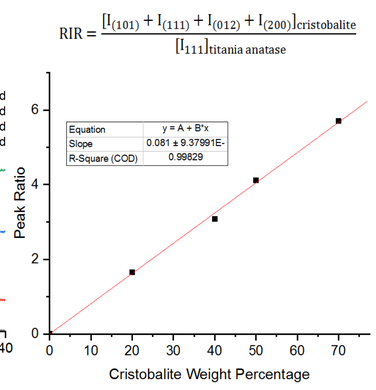
Annealing Times:
- 1250°C: 1, 5, and 9 hours
- 1300°C: 0.5, 1, 2, and 3 hours
- 1350°C: 0.5, 1.0, and 1.5 hours

Quantitative XRD Phase Analysis

Annealed samples were crushed and scanned using a Bruker D8 Focus diffractometer using a Cu Kα source operating at 40 kV and 40 mA with 0.005 step size and scan speed of 3°/min between 20°<2θ<40°. XRD data was processed using DIFFRAC.EVA to remove $K\alpha_2$ radiation and background noise.

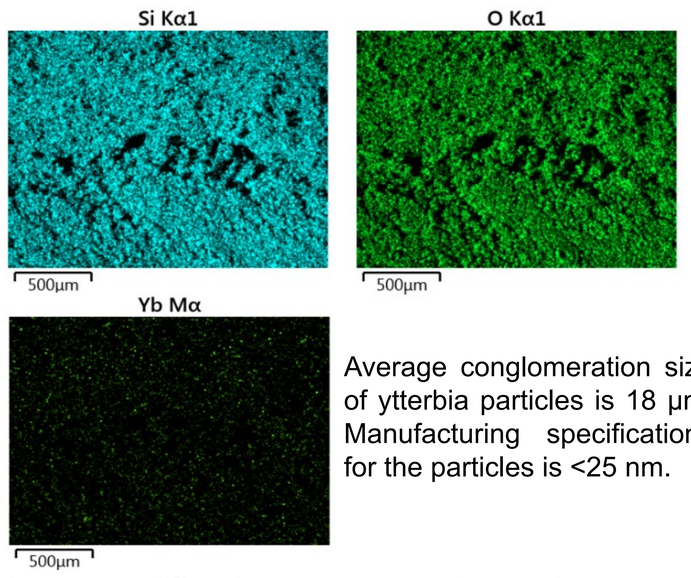
Sample crystallinity was determined using the Reference Intensity Ratio (RIR) method using a constant mass of titanium dioxide (anatase) added to each sample as an internal standard. Cristobalite content was calculated by comparing integrated peak intensities to a calibration curve. Standards were created with known masses of silica and cristobalite.





SEM Analysis

Energy dispersive X-ray spectroscopy was used to ensure homogenous mixing of REO impurities with the fused silica powder prior to annealing.

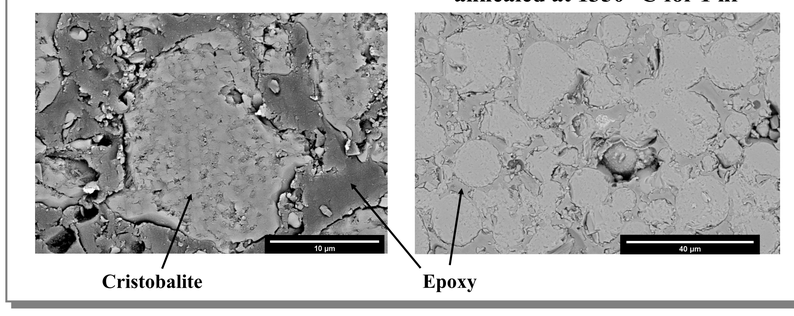


Average conglomeration size of ytterbia particles is 18 µm. Manufacturing specifications for the particles is <25 nm.

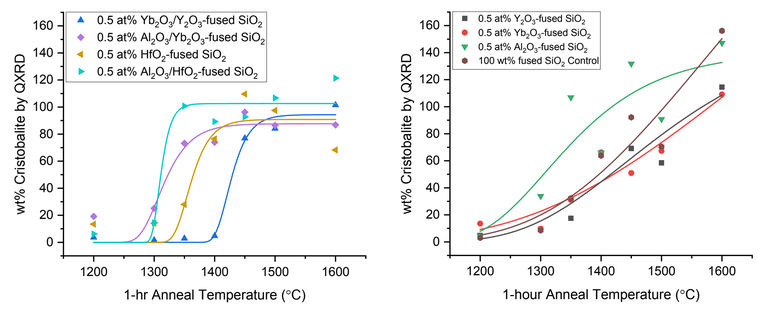
Backscatter diffraction was used to image and identify microstructural differences between phases of silica. Samples were mounted in epoxy, polished to a finish of 1 µm, and sputter-coated. The density difference between fused silica and cristobalite was expected to provide contrast.

Pure Cristobalite

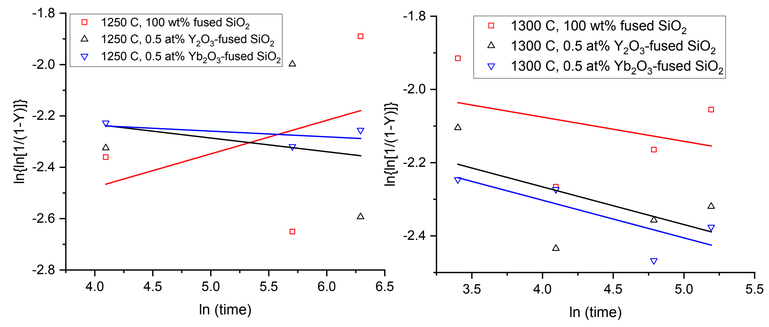
0.5 at% Yb_2O_3-silica sample annealed at 1350 °C for 1 hr

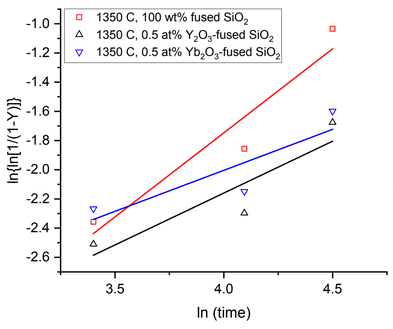


Results and Discussion



In Experiment 1, the Yb_2O_3, HfO_2, Al_2O_3/Yb_2O_3, and Al_2O_3/HfO_2 blends all match sigmoidal growth with adjusted R^2 of approximately 0.9. The results of Y_2O_3, Yb_2O_3, Al_2O_3, and the SiO_2 (control) were inconclusive and had calculated crystallinities of greater than 100%. Of the samples that show physically reasonable crystallinity, Y_2O_3/Yb_2O_3 delayed cristobalite formation until 1400 °C exposure for 1 hour. The Al_2O_3/Yb_2O_3 blend displayed the lowest-temperature onset of crystallization at approximately 1275 °C and reaching 100% crystallinity by 1400 °C.





Sample, 1350 °C series	Avrami exponent	Adjusted r^2
100 wt% fused SiO_2	1.15 ± 0.34	0.837
0.5 at% Y_2O_3-fused SiO_2	0.71 ± 0.32	0.659
0.5 at% Yb_2O_3-fused SiO_2	0.56 ± 0.31	0.529

Avrami exponents from linear fits of 1350 °C isothermal series with positive slopes are not self-consistent and cannot be used to deduce nucleation rate or growth kinetics

Samples from Experiment 2 show cristobalite formation from the isothermal series performed by Rolls-Royce. The samples held at 1350 °C followed the linearized form of the Avrami equation:

$$\ln\{-\ln[1 - Y(t)]\} = n \ln t + \ln K$$

The samples held at 1250°C and 1300°C had a negative linear fit, which made those trials inconclusive.

Noise in the data was attributed to the relatively fast XRD scan speed, which influenced the integrated peak intensities. There was only one data point per sample; repeated scans would increase confidence of results. Diffraction peaks from rare earth silicates were observed, but the phase fraction was not calculated.

Conclusions and Future Work

Samples that produced physically reasonable data in Experiment 1 showed that Y_2O_3/Yb_2O_3 impurities results in the slowest rate of cristobalite formation while samples containing Al_2O_3/HfO_3 had the fastest crystallization kinetics. Overall, the data from Experiment 2 provided no insight to the influence of rare earth oxides.

Future work includes using the Rietveld refinement method of QXRD, which could conclude in more accurate and precise results. Plasma sprayed fused silica slides were created and can be analyzed via EDS line scan to determine if diffusion occurs across the top coat-TGO interface, promoting earlier cristobalite formation.

Acknowledgements

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MSE 430-440: Materials Processing and Design