The wider adoption of SiC-based ceramic matrix composites (CMCs) for thermo-structural applications is limited in part by the challenges encountered in processing dense matrices without low melting temperature or oxidation-sensitive phases (i.e. free Si or C). Manufacturing routes utilizing polymer-derived ceramics (PDC) are being developed as a cost-effective method to manufacture CMCs with improved temperature capability. The notional approach involves repeated infiltration of the CMC preform with a preceramic polymer followed by pyrolysis to form an amorphous Si-(O-N)-C matrix. A heat treatment at a higher temperature is necessary to crystallize the PDC, which improves the thermal conductivity, thermal stability, and oxidation resistance compared to the amorphous polymer derived phase. Crystallization occurs by precipitation of SiC, C, and/or Si$_3$N$_4$ while concomitant decomposition reactions produce gaseous SiO and CO.

These crystallization processes have been studied using PDC powders, however few studies capture the effects of the mesoscale structural and chemical heterogeneities present in PIP-processed CMC matrices. The current work builds an improved understanding of PDC crystallization process in CMC-relevant geometries by examining the differences in the bulk (average) and local crystallization behavior in fiberless matrix monoliths. In conjunction with thermodynamic calculations exploring the influence of temperature and local oxygen chemical potential on the decomposition reactions, the findings provide an improved scientific basis to aid in optimizing the CMC processing protocol.

The first stage of crystallization involves rapid β-SiC precipitation throughout the bulk of the material, and appears to be insensitive to the local microstructure. Subsequent crystallization stages involve partial decomposition of PDC, producing CO and/or SiO. Because these processes involve gaseous exchange with the atmosphere, they are more directly influenced by the local microstructure. Therefore, although the bulk crystallinity quickly reaches an intermediate plateau corresponding to partial phase separation, the near-surface regions are fully crystallized more quickly than the interior regions. The implications of these effects will be discussed in the context of the manufacturing and performance of PIP-processed SiC-CMCs.

Figure 1 – (a) XRD analysis shown an increase in bulk crystallinity with increasing temperature, while (b-d) microstructure characterization shows that the rate of crystallization is strongly dependent on the local structure.