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# Crystallization behavior of polymer-derived Si-O-C for ceramic matrix composite processing

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ABSTRACT

To facilitate the development of matrix processing protocols for SiC-based ceramic matrix composites (CMC) using the polymer infiltration and pyrolysis (PIP), the crystallization behavior of a commercial Si-(O)-C polymer derived ceramic (PDC) was studied using fiberless matrix monoliths replicating the microstructure features common in PIP CMC matrices. The study examined how the processing time and temperature impact the apparent bulk (average) crystallinity as well as how microstructure features lead to variations in the local crystallization rates. The first stage of crystallization involves rapid β-SiC precipitation throughout the bulk of the material. This stage 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 are discussed in the context of the processing and performance of SiC-CMCs.

## 1. Introduction

SiC-based ceramic matrix composites (CMC) enable higher temperatures, increased component lifetimes, and improved efficiency for thermo-structural applications, e.g., in turbine engines. State of the art composites feature high-strength SiC fibers [1] coated with BN to facilitate crack bridging and fiber pullout [2,3]. The fibers are surrounded by a Si-based matrix (SiC, $Si_3N_4$, and/or Si), which distributes load and shields the fibers from the service environment [4]. However, processing dense, crystalline matrices without low melting point or oxidation-sensitive phases (i.e. free Si or C) remains a challenge [5].

One processing approach, depicted in Fig. 1, involves infiltrating the fiber preform with a preceramic polymer [6] followed by pyrolysis (e.g., 800 °C in an inert atmosphere) to produce a polymer-derived ceramic (PDC) matrix [7,8]. The polymer infiltration and pyrolysis (PIP) sequence is repeated to increase the matrix density by filling shrinkage cracks formed during prior cycles [9]. In the as-pyrolyzed state, PDCs appear amorphous by x-ray and electron diffraction. Nuclear magnetic resonance (NMR), small-angle x-ray scattering (SAXS), and Raman spectroscopy provide evidence that the local structure features $SiO_2$-like nanodomains separated by graphene-like carbon sheets [10,11]. Even though some PDC compositions offer good thermal stability in the amorphous state, a fully crystalline matrix is desired in order to increase the thermal conductivity and oxidation resistance of the CMC. To achieve the desired crystallinity, the PDC matrix must be heated above the stability limit for the initial amorphous structure. However, these higher processing temperatures can degrade the fibers and their coatings. Therefore, the processing protocol must be optimized to achieve high crystallinity while minimizing the constituent degradation.

As elaborated in Section 2, PDCs crystallize via a combination of concurrent and/or sequential phase separation and decomposition steps. These processes include precipitation of crystallites within the amorphous matrix, partial decomposition with CO and/or SiO evolution, and, depending on the local oxygen partial pressure

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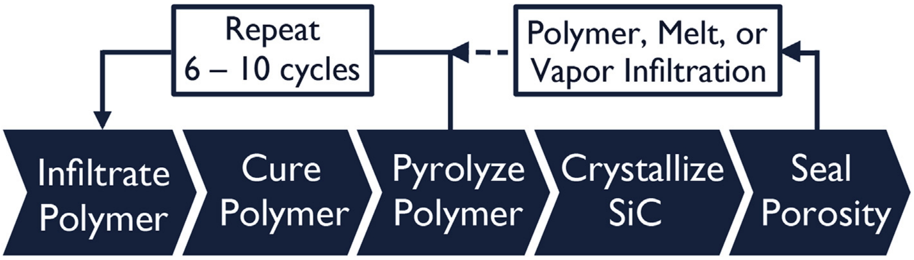

**Fig. 1.** PIP-based processing protocol to manufacture SiC-based CMCs with a hermetic crystalline matrix.

($p_{O_2}$), active or passive oxidation. This thermal evolution has been studied for select PDC compositions and processing temperatures using powders or small monoliths [10,12–21]. However, few studies capture the effects of the mesoscale structural and chemical heterogeneities present in PIP-processed CMC matrices. Thus, the objective of the current work is to build an understanding of PDC crystallization in CMC-relevant geometries in order to provide a scientific basis to aid in optimizing the processing protocol.

The heterogeneities in PIP-processed CMCs are generated by both the overall CMC architecture, including the fiber weave and local fiber packing density, and cycle-to-cycle variations in the PIP process. The inter-tow regions in woven composites typically contain larger volumes of relatively dense PDC surrounded by pores and partially filled shrinkage cracks, while there are smaller volumes of PDC and finer microcracks within the fiber tows. Therefore, the pores and cracks can range in size from nanometers to hundreds of micrometers [9,22]. Compositional heterogeneities are also possible. For instance, geometric effects influencing the constitution of the gases evolved during pyrolysis impact the local Si:C ratio. Likewise, composition changes arise because the material formed during the first PIP cycle spends more time at the pyrolysis temperature than material formed during the later cycles. Additionally, the challenges faced in preventing the virtually inevitable oxygen impurities in nominally O-free Si-C PDCs [19,20,23,24] are exacerbated when infiltrating high surface area fiber preforms containing adsorbed gases and native oxides.

The collective effect of these heterogeneities on the crystallization process and, ultimately, on the in-service CMC performance is unknown. Optimization of the CMC infiltration, pyrolysis, and crystallization protocols requires new insight into the role of compositional and microstructural heterogeneities during PDC processing. This investigation advances the understanding by examining the influence of temperature, the as-pyrolyzed composition, and geometric effects on the crystallization behavior of an industrially relevant Si-(O)-C PDC. The analysis considers both the bulk (average) and local crystallization processes in specimens replicating the microstructure features common in CMCs.

## 2. Crystallization pathways and thermodynamic insights

Within the Si-O-C composition space, shaded blue in Fig. 2, many studies have focused on families of materials that are either relatively O-rich, near $SiO_2$, or near an equimolar Si/O/C stoichiometry [10,12–17]. Other studies have examined the O-lean compositions near stoichiometric SiC [18–21], which are more relevant for processing SiC-based CMCs. The SiC crystallization process has also been studied in the context of intimately mixed $SiO_2$ and C powders, which involves similar carbothermal reduction and gas evolution processes [25]. Based on insights from these investigations, the relevant bulk composition evolution pathways for the crystallization process are illustrated in Fig. 2.

Calorimetric measurements indicate that the as-pyrolyzed PDC nanodomain structure is thermodynamically stable relative to the equivalent assemblage of SiC, graphite, and cristobalite [16,17]. Therefore, complete solid-state PDC phase separation into SiC, graphite, and cristobalite is expected to be unfavorable. In fact, at high temperatures graphite and $SiO_2$ would be expected to react yielding SiC, rather than remain in equilibrium [25]. Instead, as a polymer derived ceramic is heated above the organic-to-inorganic transition temperature, phase separation (Fig. 2(a)) proceeds

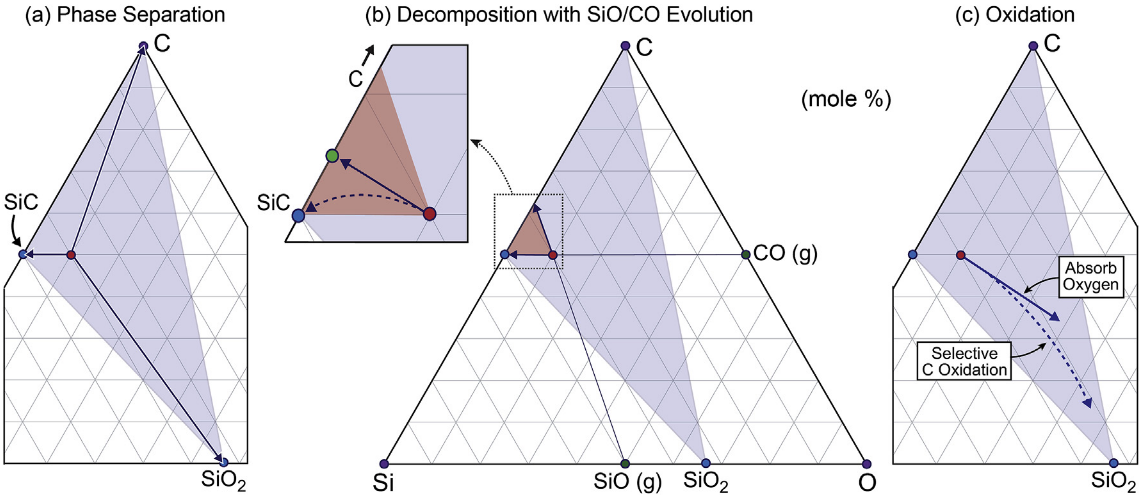

**Fig. 2.** Processes occurring during the crystallization of a PDC can include (a) solid-state phase separation into a mixture of SiC, graphite, and $SiO_2$, (b) PDC decomposition with evolved CO and SiO shifting the bulk toward the Si-C binary, or (c) oxidation of the PDC, which shifts the bulk solid composition toward $SiO_2$. The dashed pathways represent selective C oxidation by oxygen in the process gas.