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13. ABSTRACT (Maximum 200 words) This program seeks means of fabricating thick cross-section monolithic and composite ceramic components using polymeric ceramic precursors, thereby realizing potential processing and quality advantages. This program's strategy for overcoming longstanding problems is based on developing and maintaining a precisely controlled interconnected pore structure within the reacting part, thus providing a pathway through which gaseous reaction products can escape without damaging the part and into which gaseous reactants can freely penetrate, enabling synthesis reactions to proceed uniformly at maximum rates. The approach taken is based on filling the void space within solid phase reactants because this option offers important opportunities for minimizing both shrinkage and residual porosity. During the past year this research has: (1) investigated whether inert fillers can be made to act as nuclei for reaction products formed from the polymeric ceramic precursors, (2) sought means to prevent migration of the reactive binders during drying, and (3) made reaction formed silicon nitride matrix composite parts using mullite fibers. Results indicate that the approach is viable.				
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ONR CONTRACT INFORMATION

Contract Title: Synthesis of Net-Shape Ceramic Matrix Composites from
Phase Separated Polymeric Precursors

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Objective and Approach

This program's principal goal is to make it possible to fabricate thick cross-section monolithic and composite ceramic components using polymeric ceramic precursors. Potentially polymeric precursors offer important advantages in terms of forming rates, part complexity and flaw dimensions. However, to date low densities and excessive shrinkage have prevented realization of these advantages for conventionally formed parts; excessive manufacturing costs and inconsistent quality have prevented general implementation of infiltration-pyrolysis processes for CMC's.

This program's strategy is based on developing and maintaining a precisely controlled interconnected pore structure within the reacting part, thus providing a pathway through which gaseous reaction products can escape without damaging the part and into which gaseous reactants can freely penetrate, enabling synthesis reactions to proceed uniformly at maximum rates. Precisely controlled pore structures may be produced (1) by replicating a preexisting pore structure with the reactive polymer, (2) by removing one phase from a phase separated microstructure in the polymeric precursor, or (3) by using inherently porous reactants such as sol-gels.

This research has focused on the first approach, in which a reactive polymer is made to fill voids within a porous solid phase. We have explored three types of porous solids; these are: (1) a fugitive material as is commonly used to form reticulated structures, (2) an inert filler which does not participate in the chemical reaction, but which may provide preferential sites for nucleation, and (3) a solid reactant which participates in the chemical reaction.

This research has emphasized solid phase reactants because this option offers important opportunities for minimizing both shrinkage and residual porosity. When compared with using either no filler or inert powder fillers, our previous analyses showed that density levels could be increased significantly by using preceramic polymers as binders for reactive powders. These predictions were confirmed experimentally using polysilazane binders and Si powders that were fired in nitriding atmospheres. Silicon powders packed to a volumetric density of 66% with 12% dried polysilazane binder converted to 83% dense Si_3N_4 samples in a single firing step. Use of an inert filler has also been explored because it offers opportunities for enhancing crystallization and significantly reduces the average cost of raw materials.

During the past year this research has addressed three specific topics. Inert fillers have been investigated to determine whether they can be made to act as nuclei for reaction products formed from the polymeric ceramic precursors. Means were sought to prevent migration of the reactive binders during drying. Finally, reaction formed Si_3N_4 matrix composite parts were made using mullite fibers to determine whether oxidation resistant fibers can be substituted for the

SiC fiber reinforcements that have been emphasized for nonoxide matrix CMC's.

Significant results in the past year

Crystallization: For high temperature applications, it is essential that the preceramic polymer convert to crystalline reaction product(s) within temperature limits defined by damaging interactions between CMC phases. Our previous results strongly suggest that the onset of crystallization as well as the reaction path are both favorably influenced by the presence of seed crystals which enhance the nucleation of product phase(s). For Si_3N_4 synthesized in a nitriding atmosphere from mixtures of polysilazane and Si powder, it is believed that crystalline Si_3N_4 originating from the nitridation of the Si particles serve as nuclei for the reaction product originating from the preceramic polymer. Others have speculated that Si, produced during pyrolysis of neat polysilazanes in a NH_3 atmosphere, functioned in the same manner. Similarly enhanced crystallization of polymeric reaction products has been observed at MIT and elsewhere when reactions begin to occur between Si particles and carbon originating from polycarbosilane binders.

While enhanced crystallization by these routes represents an important improvement, practical utilization is not easily achieved because formation of nucleation sites is dependent on complex reaction sequences. Improved control is anticipated if the seed crystals can be introduced by simply adding them to the reactant. Current experiments tested the viability of using inert powders as seeds by investigating the crystallization of the polymer reaction product in the presence of high purity Si_3N_4 powder.

X-ray diffraction (XRD) analysis shows that samples made of mixtures of Si and polysilazane were completely crystalline after heating to 1400°C in N_2 ; while in contrast, samples of polysilazane were completely amorphous after the same heat treatment. Differential thermal analysis (DTA) of mixtures of Si powder and polysilazane to 1550°C revealed only exothermic events at temperatures ($1200 - 1400^\circ\text{C}$) corresponding to weight gains dominated by the nitridation of the silicon powder. Though not interpreted mechanistically, the polymer product crystallized completely to Si_3N_4 while the Si powder nitrided. DTA analyses of polysilazane- Si_3N_4 powder mixtures revealed only weak exothermic events extending over a broad range of temperatures below normal nitriding and crystallization levels. TEM and XRD analyses of these samples are continuing.

Polymer migration: Migration during drying is commonly encountered with fugitive binders that are dissolved in solvents. Residual stresses and warpage are the most common serious consequences of this phenomena for fugitive binders. Reactive binders are subject not only to these problems but also to density gradients resulting from inhomogeneous distribution of the reaction products derived from the binders. The problem is exacerbated when average

binder concentrations approach maximum permissible levels, because locally elevated concentrations will block nearby pores thus preventing complete reaction.

Binder migration has been observed in reaction formed (nitrided) samples made with Si powder and polysilazane binder. For these cases, excess binder concentrated in internal regions as the solvent-gas interface receded into the body. In a few extreme cases, inner regions did not nitride completely due to pore blockage.

We identified a practical option for eliminating binder migration. Green parts are formed by using a liquid-phase monomer or a soluble-polymer solvent solution. After completing forming operations, the spatial distribution of the preceramic polymer is established and fixed by cross-linking the monomer or soluble-polymer in situ. This approach rigidizes the polymer structure before drying. When the monomer is used, it permits more preceramic polymer to be incorporated into the part than traditional approaches based on polymer-solvent solutions. This processing option has been investigated by substituting a cyclic silazane monomer for a typical polymer solution.

Two modified sample forming processes were investigated; both were polymerized (150°C) in containers which minimized vapor losses. First, inert gas pressure was used to force the monomer into dry Si powder compacts. Infiltration was not complete and, also, the infiltrated region was macroscopically cracked after nitridation. Second, Si powder was mixed with excess monomer and the excess liquid was extruded as the powder was compressed in dies used for colloidal pressing. This approach filled all available pore space with monomer. These samples were nitrided successfully without cracking as part of the crystallization study.

Based on successfully rigidizing the monomer in situ and nitriding the parts without cracking, further process modifications are being developed. These changes will increase the porosity level to facilitate mass transport within the part during pyrolysis and reaction processes. Monomer- and polymer-solvent solutions will be subjected to cross-linking heat treatments in a closed pressure vessel which maintains an atmosphere that is saturated with the solvent. This process will prevent solvent loss from the part during cross-linking, then allow its precise removal after the binder is polymerized.

Composites: Experimental results and analyses have shown that SiC reinforcement fibers will not survive for acceptable periods after matrix cracking in the high temperature oxidizing atmospheres that are projected for engine applications. Mullite represents the only oxide which is available in the form of high quality fibers, and which exhibits acceptable high temperature mechanical properties, and whose thermal expansion coefficient is matched to Si₃N₄ and

SiC matrices. Melt grown, nominally single crystal, mullite fibers were contributed by Dr. Ali Sayir at NASA LERC and by Dr. Winfield Perry at Advanced Crystal Products for incorporation into RBSN matrices. Unidirectional RBSN matrix composites were made with both fiber types.

Results were very encouraging. No adverse effect was noted on the nitriding kinetics of the high purity silane derived Si powders. Fracture surfaces containing both types of fibers exhibited pullout and no evidence of interactions between the fiber surfaces and the matrices. Pushout and tensile experiments showed that the fibers slipped relative to the matrix, but appeared restricted by the irregularities on the faceted fibers. Experimental results gave no indication of problems which would make the composite impractical.

The results of this research are summarized in the attached preprint of a paper entitled "Mullite Fiber Reinforced Reaction Bonded Si₃N₄ Composites" which will be published in the Ceramic Engineering & Science Proceedings of the 20th Annual Conference on Composites, Advanced Ceramics, Materials, and Structures.

Plans for next year's research

Continuing research next year will focus on the three following topic areas.

- (1) Identify means of preventing migration of reactive binders during drying operations. This issue is particularly important when making reaction formed parts with maximum density levels.
- (2) Reactive binders and solvents satisfying (1) will be sought which do not inhibit the Si powder nitridation kinetics. While crystalline SiC reinforcement fibers are not degraded by nitriding temperatures (1375-1400°C) generally used to ensure complete nitridation of polymer-exposed and air-exposed Si powders, the lower cost polymer derived SiC fibers and polycrystalline mullite (commercially available) fibers are both irreversibly damaged when exposed to temperatures in excess of 1225-1250°C. Maximum utilization of the opportunities made possible by these reaction forming processes for CMC's requires restoration of Si particle surface conditions which permit complete nitridation for $T \leq 1250^\circ\text{C}$.
- (3) The crystallization kinetics and microstructures of the polymeric reaction products will be studied. Fully crystalline reaction products are highly desirable based on superior high temperature mechanical properties, chemical durability and thermal conductivity.
- (4) Pending a continued collaboration with Dr. A. Sayir at NASA Lewis, mechanical properties of mullite fiber CMC's will be measured and related to microstructural features.