INVESTIGATION ON PRECERAMIC POLYMERS FOR MULLITE MATRIX COMPOSITES AND CERAMIC FOAMS FOR THERMAL PROTECTION APPLICATIONS

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SANDHYA G NAIR
SC19D015

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF SPACE SCIENCE AND TECHNOLOGY
THIRUVANANTHAPURAM

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ABSTRACT

Hypersonic air-breathing vehicles are envisioned as the future of aerospace transportation. Developing thermal protection materials is crucial for realizing these vehicles. These materials need to be thermally stable, inherently resistant to oxidation, and capable of retaining form and strength at high temperatures. Additionally, they should have low thermal conductivity and be lightweight to meet the demands of vehicle designers.

Mullite ceramics exhibit excellent thermal stability and creep resistance in oxygen-rich, high-temperature environments. They also have low thermal conductivity and maintain good strength at elevated temperatures. Because of these qualities, oxide fiber-reinforced mullite composites are extensively studied for thermal protection system (TPS) applications. However, conventional processing methods like diphasic sol-gel or ceramic slurry deposition have drawbacks such as non-uniform matrix deposition, high-pressure requirements for infiltration, and potential damage to reinforcements during high-temperature processing.

Addressing these challenges necessitates the exploration of alternative low-temperature processing methods for Oxide Ceramic Matrix Composites (OCMCs). The polymer-derived ceramic route has emerged as a promising approach for low-temperature ceramic processing. This method allows for precise distribution of elements at the nano-level, pressureless sintering, and improved control over ceramic composition. By facilitating the low-temperature formation of desired ceramic phases, this approach enables the processing of OCMCs at relatively low temperatures, thereby reducing the risk of damage to oxide reinforcements. Considering the above aspects, it is important to realize novel resinous monophasic precursor materials with high ceramic yield which can give mullite and ZrO_2-mullite phase at relatively low processing temperatures, enabling the processing of OCMCs at a low processing temperature.

Monophasic mullite precursors, namely aluminosiloxanes (AS) were synthesized in resinous by a novel synthetic route. The reaction mechanism was confirmed by the identification of reaction by-products via GC-MS. Aluminosiloxanes were characterized by FT-IR, NMR, and elemental analyses. Spectral analysis confirms the presence of Si-O-Al bonds in all the precursors and also validates the incorporation of more aluminium via Si-O-Al bonds with increasing Al/Si mole ratio in the precursor. FT-IR and NMR data also attest the precursor level homogeneity in all the samples. The effect of Al/Si ratio on the ceramic conversion was studied and the results showed that the aluminosiloxanes are capable of giving high ceramic residue qualifying them as ceramic matrix precursors for OCMCs. All the precursors showed the formation of mullite at 900°C. This low temperature mullite formation is a key factor in developing OCMCs without fiber damage. The results obtained from the study show that the composition of the ceramic can be controlled between a silica rich mullite phase and near-stoichiometric mullite phase by suitably selecting the Al/Si monomer feed ratio of the precursors. This aspect provides a greater scope for designing application-specific ceramic matrices for space applications.

Zironia doping in mullite ceramic can significantly improve the properties of mullite. In order to incorporate ZrO_2 in the mullite ceramic phase, Zr modification of the aluminosiloxane was attempted. Aluminosiloxane (AS) is chemically modified with zirconium propoxide (ZrP) to synthesize zirconoaluminosiloxanes (ZAS) in the resinous form. The effect of zirconium incorporation in the aluminosilicate network is studied by FT-IR, NMR, and TG/DTA analysis. ^{29}Si-NMR and ^{27}Al-NMR spectra clearly indicate that zirconium is chemically bonded to the aluminosilicate network and the network connectivity increases with increase in zirconium content. ^{27}Al-`NMR also reveals the progressive distortion of octahedral symmetry of AlO_6 due to zirconium incorporation, validating the insertion of Zr through Al-O-Zr bonds where Al is four coordinated. These observations attest the monophasic nature and the chemical homogeneity of the synthesized precursors, which is the main factor contributing to the low crystallization of ceramic phases. Ceramic conversion studies of the precursors confirmed the formation of crystalline zirconia/mullite ceramic phases at a low temperature of 900°C. The XRD and microstructure analysis by SEM/EDX indicated that the mullite crystallization can be controlled by zirconia incorporation. This effect is discussed in terms of the occupancy of zirconia either as intra-granular or inter-granular particles.

High-temperature thermal protection tiles are essentially required for heat management in hypersonic vehicles. Investigation on the fabrication of two types of easily processable, lightweight OCMC tiles via polymer infiltration and pyrolysis route (PIP) is disclosed. Two types of OCMC tiles were developed: OCMC01, composed of fibrous alumina reinforcement and mullite derived from Aluminosiloxane (AS32), and OCMC02, composed of fibrous alumina reinforcement and zirconia-mullite derived from zirconaluminosiloxane (ZAS17). To meet lightweight requirements, the bulk density of the tiles was adjusted to 0.5g/cc by controlling the number of PIP cycles. Microstructure analysis via SEM confirmed a porous structure which helps in reducing thermal conductivity. OCMC02 exhibited superior thermo-mechanical properties compared to OCMC01 due to the presence of zirconia. End use evaluation for hypersonic vehicle applications showed both OCMC01 and OCMC02 enduring high heat fluxes of 18W/cm^2 (ramp 1) and 46W/cm^2 (ramp 3) for 550 seconds without damage, indicating their potential for use in hypersonic air-breathing vehicle air intake ramp area.

A comprehensive investigation was also carried out on the preparation and characterization of reticulated cellular ceramic structures using aluminosiloxane and zirconoaluminosiloxane resins using polyurethane (PU) foam template. By employing dual impregnation and squeezing loads, ample quantity of precursors is deposited onto the PU template, preventing foam collapse during template burnout and ceramization. The presence of non-porous struts and ligaments in the foam indicates successful wetting and homogenization of the PU foam template with the mullite precursor resins. XRD analysis reveals the devitrification of silica to cristobalite at 1500°C and its verification at 1600°C. The vitrification of cristobalite is found to facilitate mullite densification and grain growth through liquid phase sintering. SEM images at high magnification depict clearly defined needle-shaped grains in foams sintered at 1600°C, with doped zirconia observed as tetragonal nanocrystals at the boundaries of mullite grains. Foams with porosity ranging from 83% to 95.2% demonstrate compressive strengths and thermal conductivities within the ranges of 0.11 to 0.4 MPa and 0.15 to 0.08 $Wm^{1}K^{-1}$, respectively.

The results of this study are anticipated to contribute new insights to the field of thermal protection systems. The creation of innovative single-phase precursors, integration of zirconia, and exploration of alternative processing techniques hold potential for addressing the challenges related to thermal protection materials for hypersonic air-breathing vehicles.