Novel Ceramics and Metal-Ceramic Composites via Fused Deposition Process

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Abstract

Indirect fused deposition process is utilized to fabricate controlled porosity ceramic structures using alumina, mullite, zirconia, LSCF-perovskite, tricalcium phosphate and hydroxyapatite, where pore size, pore shape and pore connectivity are varied from one end to the other end of the parts. Some of these porous ceramics are then infiltrated with metals via pressureless reactive metal infiltration to form novel metal-ceramic composites. This paper will describe processing, structures of various porous and metal-infiltrated composites and their physical and mechanical properties.

Introduction

Ceramic materials possess high strength, high corrosion and oxidation resistance, excellent high temperature properties, but are brittle. The lack of toughness in ceramic materials due to their strong ionic and/or covalent bonding limits their use in numerous structural applications. Development of ceramic based composites work was started to overcome this inherent problem by incorporating ductile phases or using unidirectional ceramic fibers or ceramic cloth into another ceramics. As various novel composite materials with higher toughness were developed, several processing techniques were also invented to fabricate these materials.

In this work, novel 3D honeycomb porous ceramic structures were fabricated using indirect fused deposition (FD) process. For the past three decades, various processing techniques have been utilized to fabricate porous ceramic materials [1-4]. Unfortunately, all of these processes form structures with randomly arranged pores having a wide variety of sizes and with limited flexibility to control pore volumes and porosity distribution in the final structure. Using indirect FD, controlled porosity structures were fabricated where pore size, pore volume and porosity distributions were precisely controlled [5-6]. Different materials were used to process these structures for various applications. Porous alumina and mullite ceramics were fabricated to form interpenetrating phase metal-ceramic composites. Porous hydroxyapatite (HAp), tricalcium phosphate (TCP) and alumina structures were fabricated for bone graft application. Porous LSCF ceramics were fabricated for catalytic membrane applications and porous PZT structures for transducer and actuators. All of these structures were fabricated with uniform or functionally gradient porosity where the volume fraction porosity varies from one end of the structures to the other end. **Figure 1a, b and c** show some of the porous structures having uniform and gradient porosity.

Pressureless reactive and non-reactive metal infiltration processes were used to infiltrate the porous alumina and mullite ceramic preforms to fabricate metal-ceramic composites with a

controlled shape as well as microstructure. Reactive synthesis of composites offers the advantages of net-shape structure processing with the control of the final microstructure. Several researchers have proposed the use of molten aluminum and either silica glass or aluminosilicate ceramics to obtain alumina/metal composites by reactive penetration [7-9]. Reactions between liquid metal and ceramic oxides may be of the type $4M + 3SiO_2 = 2M_2O_3 + 3Si$, where M is a trivalent metal and the thermodynamic criterion being that at the processing conditions, the Gibbs free energy of the reaction is negative [10]. For both dense and porous ceramic substrates, reactive infiltration to take place it is necessary to reach a critical temperature. Once the infiltration starts, it is faster with higher porosity and smaller particle size. This paper describes processing and mechanical characterization of alumina-aluminum and mullite-aluminum composites.

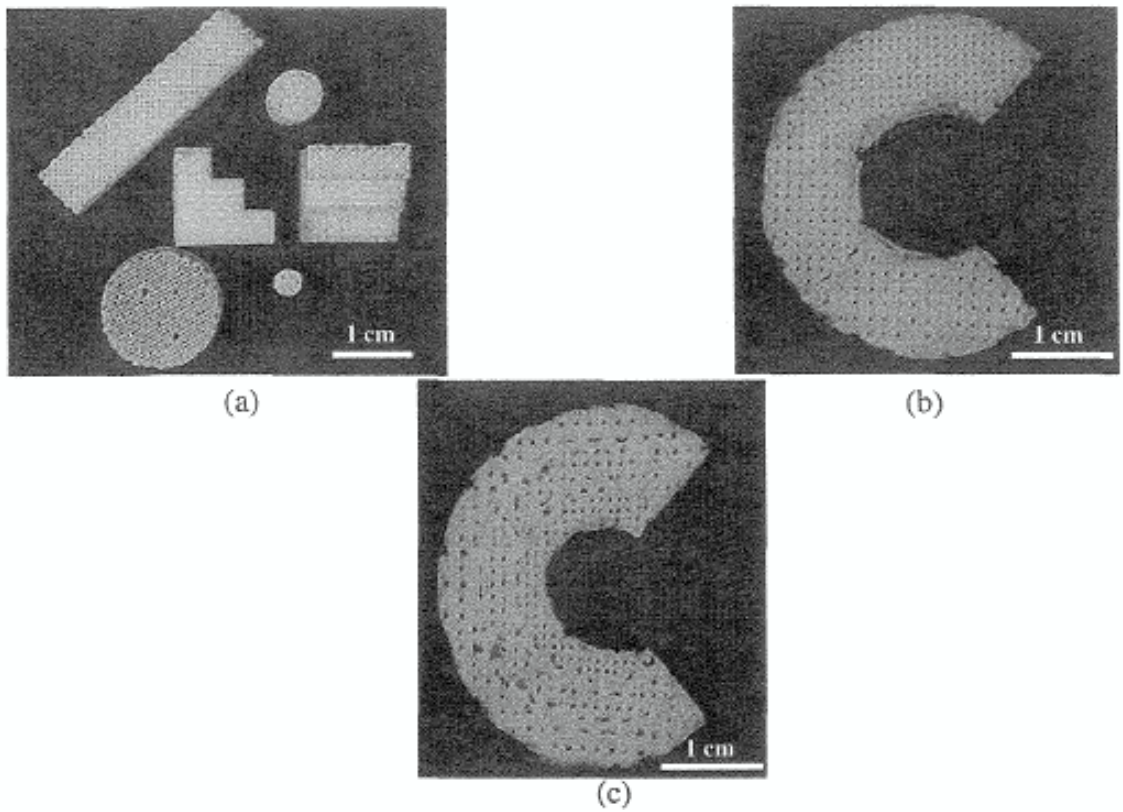


Figure 1: Porous 3D honeycomb structures processed via indirect FD process. (a) Structures having various shapes with uniform porosity; (b) structure with a gradient porosity microstructure from one end to the other and (c) structure with a gradient porosity microstructure from center to the outside of the C-ring (porosity gradient in radial direction).

Processing

Indirect FD process was used to fabricate porous ceramic structures. In this process, FDM 1650 was used to make polymeric molds having the negative of the desired structure and then was infiltrated with water based ceramic slurry. Infiltrated structures were dried for three to four days and then subjected to a binder removal and sintering cycle using a high temperature muffle furnace in furnace air environment. Structures with various pore size, pore volumes and porosity gradients were fabricated using this process.

Alumina and mullite porous ceramic preforms were then infiltrated with Al metal. In case of reactive metal infiltration, the process has two steps: infiltration and reaction. The infiltration and reaction steps can be independent of each other or can take place simultaneously. For the case of mullite-Al composites, it is expected that mullite will react with Al and form an alumina-aluminum composite via a displacement reaction given by:

$$3 \text{ Mullite } (3Al_2O_3, 2SiO_2) + 8 \text{ Al} \quad => \quad 13 \ Al_2O_3 + 6 \text{ Si}$$

Aluminum metal was infiltrated into porous preforms at 850^{0}C temperature or higher. Porous ceramic preforms were dipped into the crucible of molten Al alloy at 750^{0}C and furnace temperature was raised to a temperature at 850^{0}C or higher. At that temperature, low viscosity molten Al metal filled the porous ceramic network and formed 3-3 mullite-Al composite, where both mullite and Al were connected to themselves in all three directions. Once the metal infiltration was over, the assembly was cooled to 700^{0}C and the composite was taken out of the crucible. As the composite was taken out of the molten Al alloy, the shape of the porous ceramic became the shape of the composite. As the shape of the porous ceramic preform can be controlled by RP, this process has the flexibility to fabricate near-net-shape part with controlled microstructures.

For mullite-Al composites, it was found the complete infiltration can be achieved by going up to 850^{0}C, but there was no reaction between mulite and Al. **Figure 2a** shows the x-ray diffraction patterns for mullite ceramic preform and composites infiltrated at 900, 950 and 1000^{0}C. It can be observed that there was no reaction between mullite and Al, and the structure forms a mullite-Al composite. **Figure 2b** shows similar x-ray diffraction patterns for composites processed at 1050, 1100 and 1150^{0}C and compared with mullite ceramic preform. It can be observed that the reaction between Al and mullite starts around 1050^{0}C and completes by 1150^{0}C and it forms α-alumina-Al metal-ceramic composite.

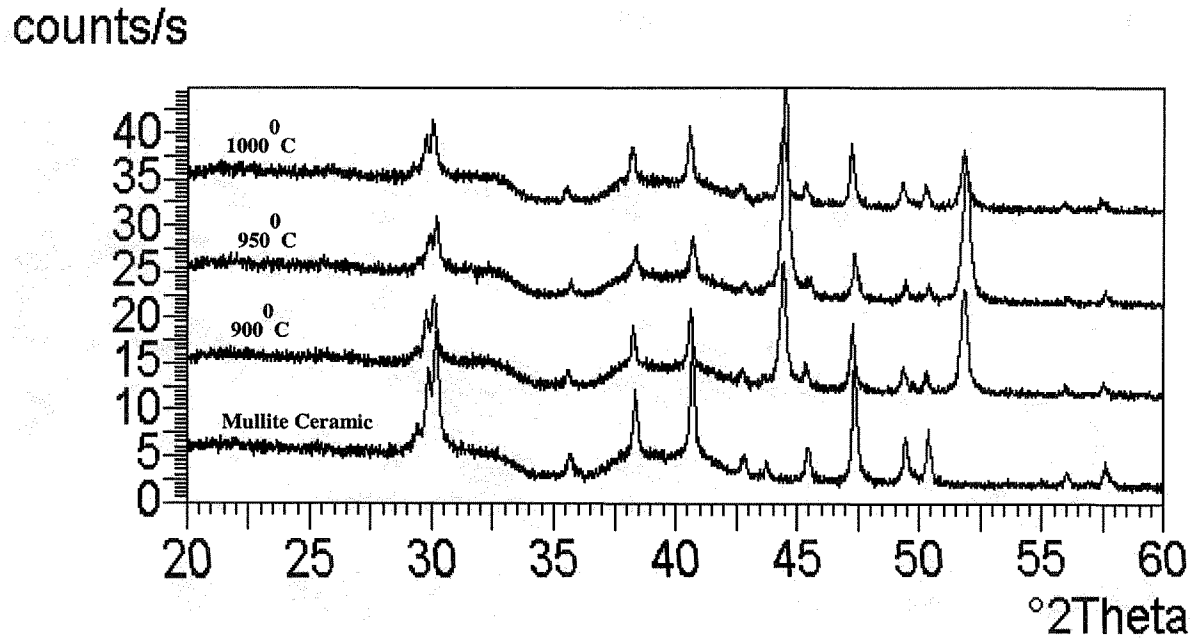


Figure 2a: X-ray diffraction patterns for porous mullite ceramic and Al infiltrated composites. Al metal was infiltrated at 900, 950 and 1000^{0}C for one hour to form the composite.

In the case of pressureless non-reactive metal infiltration process, there is no reaction step, but only the infiltration of molten metal is involved. Low temperature Al metal infiltration of mullite ceramic preforms can serve as an example of non-reactive metal infiltration process. In this work, porous alumina ceramic preforms were infiltrated with molten Al and Cu metals to form Al-alumina and Cu-alumina composites. This process involves only infiltration of molten metal, but no reaction between Al and Cu with alumina. **Figure 3a and b** show the porous alumina preforms and a Cu infiltrated microstructure.

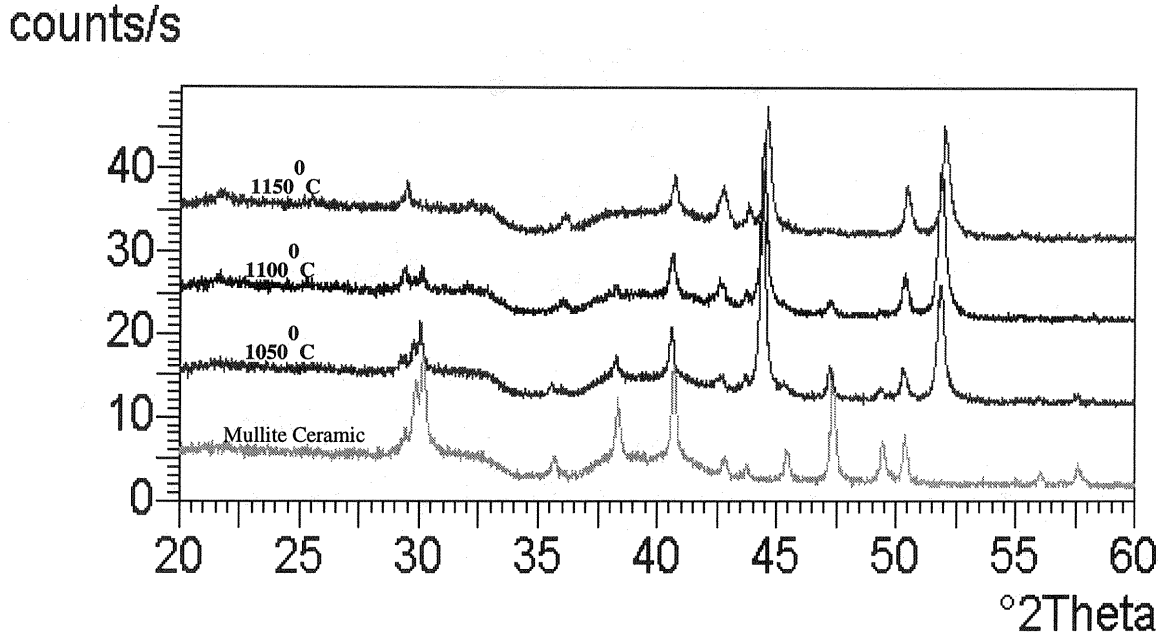
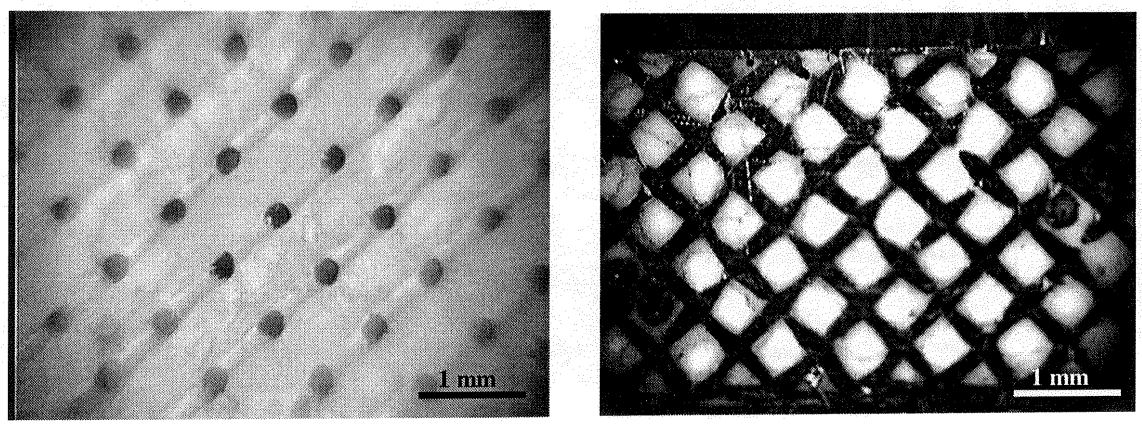


Figure 2b: X-ray diffraction patterns for porous mullite ceramic and Al infiltrated composites. Al metal was infiltrated at 1050, 1100 and 1150^{0}C for one hour to form the composite.



(a) (b)

Figure 3: (a) Top view of porous alumina ceramic preform and (b) top view of the Cu infiltrated alumina ceramic composites.

Results and Discussion

Composites via non-reactive infiltration process: Al-alumina and Cu-alumina composites that were processed via non-reactive metal infiltration process were all cracked during polishing or cutting operation. The cracking were observed in ceramics as can be seen in Figure 4. The coefficient of thermal expansion (CTE) mismatch between metal and ceramic were high and resulted high tensile residual stress in ceramic during cooling from the processing temperature. The inherent high residual stress caused cracking in alumina ceramic during any further operation with these composites.

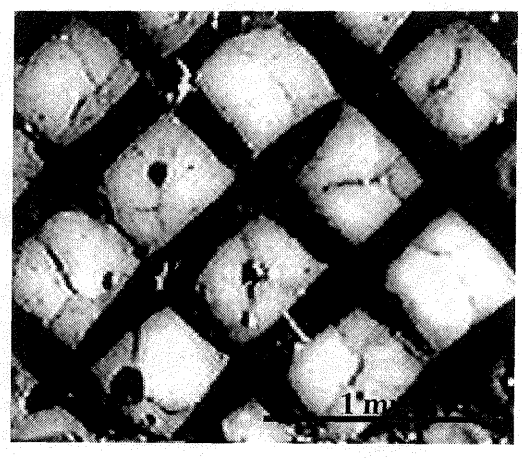
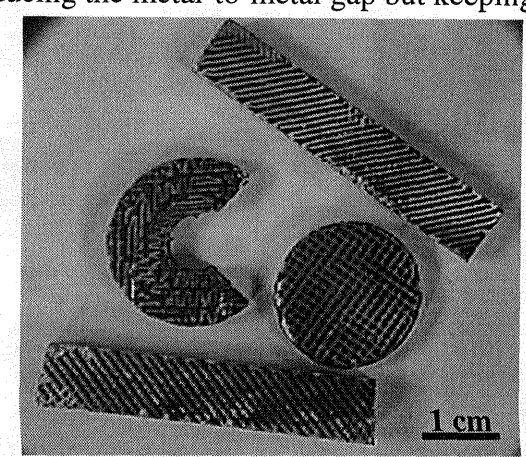
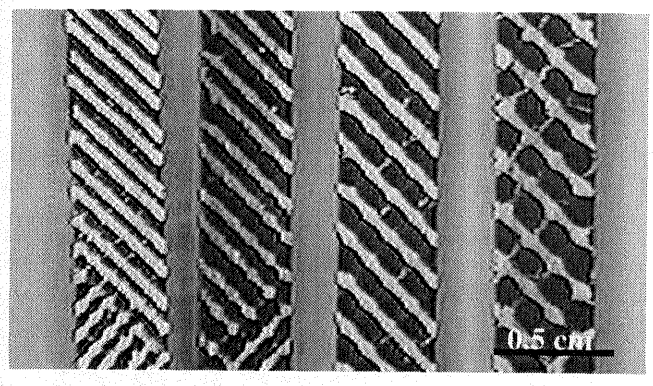


Figure 4: Alumina-Cu metal-ceramic composites showed extensive cracking during post processing in ceramics due to high residual stress.

Composites via reactive infiltration process: Mullite-Al composites were processed via reactive metal infiltration process. Porous ceramic preforms of mullite having different volume fractions of porosity were infiltrated with Al metals to form composites with different amounts of metal in it. Figure 5a shows various shapes of composites processed with mullite ceramic preforms and Figure 5b shows increasing volume fraction metals in these composites by reducing the metal-to-metal gap but keeping the width of the metal constant.



(a)



(b)

Figure 5: (a) Various mullite-Al composites processed via Al metal infiltration of porous mullite ceramic preforms. (b) Mullite-Al composites having different amount of metals.

Optical microstructures of the infiltrated composites show complete metal infiltration of the ceramic preforms. Figure 6 shows an optical micrograph of the infiltrated mullite-Al composite. Higher magnification microstructures revealed that even the micropores due to incomplete sintering was also filled with Al metal during infiltration. Microhardness measurements on the polished surfaces of the composites were made using a Vicker's indenter as a function of processing temperature. Hardness of the metal remain same for all the cases, while for ceramics, it increased from 1200 VHN to 1550 VHN due to phase transformation of mullite to α-alumina. These composite samples did not show any cracking and could be machined with regular machine tools.

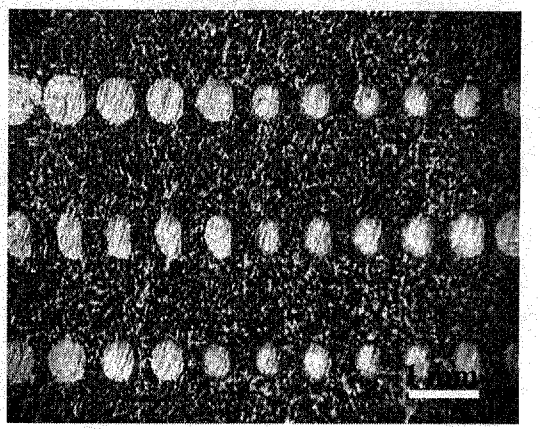
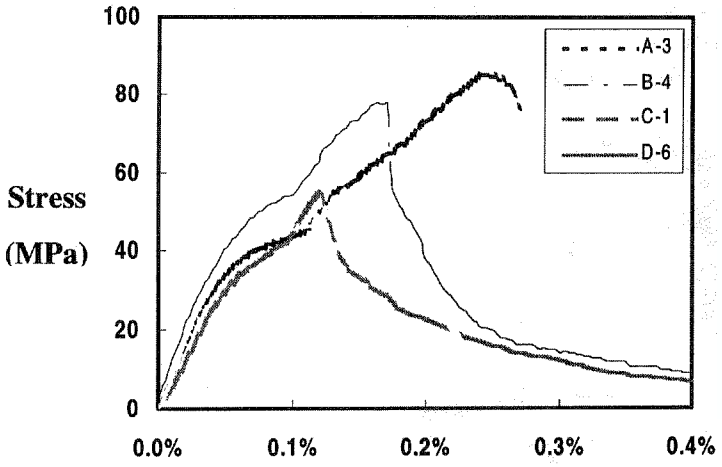
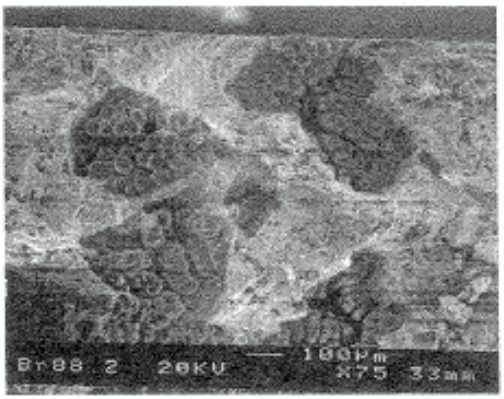


Figure 6: Low magnification optical micrograph shows the complete infiltration of pores in mullite ceramic preform by Al metal (bright areas are Al metal).



(a)



(b)

Figure 7: (a) Stress-strain curves for mullite-Al metal ceramic composites with different volume fractions of metals. (b) Low magnification fracture surface showing different types of failure for metals and ceramics.

Volume % / Strength	43% Metal	33% Metal	27% Metal	24% Metal
MOR (MPa)	87	78	50	52
Bending Modulus (GPa)	63	67	71	75

Table I: Mechanical properties of mullite-Al composites.

Four point bend flexural tests were conducted with four different types of mullite-Al composites having metal contents varied from 24% to 43% using an Instron load frame. Tests were conducted under stroke control using a 0.1mm/minute stroke rate. Flexural strengths and bending modulus are shown in Table I. It can be seen that as the metal content decreased, the bending modulus and strength increased. Increasing bending modulus can be explained due to increase in ceramic content in the composite. Figure 7a shows stress-strain curves for these composites where A means 43% metal sample and D means 24% metal. All four curves show two stages of failures and initial failure of the samples took place at ~0.1% strain. Reported bending modulus numbers were the initial modulus values. After the initial failure, there was change in modulus in the composites. Composites with higher metal contents sustained a higher load to final failure than composites with lower metal contents. The data suggests that higher metal content composites are more damage tolerant. Figure 7b shows a low magnification fracture surface of a 43% metal content sample. It can be seen that the ceramics and metal surfaces show two different types fracture surfaces. While ceramics showed a typical flat brittle failure feature with micropores, metal surfaces show ductile dimples. There was no metal pullout in all the fracture surfaces suggesting that the bonding between metals and ceramics were strong. Other samples showed a similar failure behavior.

Conclusions

Novel 3D honeycomb porous ceramic structures were fabricated using indirect FD process with various materials for applications in structural, bio-medical and piezoelectric areas. Among them, alumina and mullite ceramic preforms were used to form metal-ceramic composites having controlled macro and microstructures. Reactive and non-reactive metal infiltration processes were used to infiltrate molten Al and Cu metals to form the composites. Though composites formed via non-reactive infiltration with alumina ceramic preforms showed extensive cracking due to CTE mismatch, but composites formed with mullite ceramics did not show similar trends. Composites formed with mullite ceramic preforms showed that metal infiltration can be performed as low as 850^0C, but reaction between mullite and Al starts around 1050^0C and forms an α-alumina-Al composite. Four point bend flexural strengths of mullite-Al composites as a function of volume fraction metal present showed that bending modulus increases as metal content decreases and flexural strength increases as metal content increases. Fracture surfaces of the composite reveal two completely different types of fracture behavior.

Ceramic surface showed brittle flat fracture surface while the metal surface showed ductile dimples. The process allows for processing of composites with tailored microstructure along with physical and mechanical properties.

Acknowledgments

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