



Evolution of *In-Situ* Nano-Pores during Friction Stir Processing of Polymer Derived Ceramic Reinforced Metal Matrix Composites

Ajay Kumar P^{1*} and Satish V. Kailas²

Abstract

Nano-porous ceramics have potential applications as diverse as biomedical implants, catalysis, and armors. This work shows that *in-situ* Nano-porous Polymer Derived Ceramics (PDC) can be produced in Metal Matrix Composites (MMCs) using solid state Friction Stir Processing (FSP). Direct insertion of cross-linked polymer into the metal by FSP in solid state is a significant step toward inserting different chemistry of polymer precursors to generate a variety of *in-situ* porous structures in Polymer Derived (PD)-MMC. The PDC route is an efficient and cost effective way to produce SiCN-based PD-MMC and tailored pore architecture suitable for high temperature applications. Microstructural observations indicate a uniform distribution of ~100 nm size pores in the ceramic phase after pyrolysis.

Keywords

Polymer derived ceramics; Porous materials; Friction Stir Processing; Metallic composites

Introduction

Polymer Derived Ceramics (PDCs) represent a unique class of high-temperature stable materials synthesized directly by the thermal decomposition of polymers. PD silicon carbonitride (Si-C-N) ceramics are candidate materials for high temperature structural and functional applications in the form of fibers [1], protective coatings [2], fiber and particulate-reinforced composites [3]. In air, they are stable up to 1500°C. The synthesis of the materials involves cross-linking and/or pyrolysis of suitable organo-silicon precursor polymers in inert atmosphere, leading to ceramics with high purity, controlled structure and chemical composition [4]. Fabrication of the non-oxide Polymer Derived Porous Ceramics (PDPC) via the method of PDC is a novel technique. Furthermore, PDPC can be synthesized at a temperature as low as 1000°C free of any additives, and cost-efficient manners which cannot be performed by the powder-route technique. Porous ceramics possess number of favorable properties which combine the merits of ceramics and porous materials such as light weight, low density, low thermal conductivity, low dielectric

constant, thermal stability, high specific strength, high specific surface area, high porosity, high permeability, high wear resistance, and high resistance to chemical attack [5].

FSP has successfully evolved as an alternative technique for fabricating MMCs [6]. FSP depends on the standards of Friction Stir Welding (FSW) [7]. In FSW, a rotating tool with a pin and a shoulder are inserted into the material to be joined and traversed along the line of the joint. The friction between the tool and the work piece resulting in localized heating that softens and plasticizes the material. In the FSP of MMCs, the material undergoes intense plastic deformation resulting in the mixing of ceramic particles and the metal. FSP also results in significant grain refinement [8] and has also been used to homogenize the microstructure of Nano composites [9].

Our previous published work reported the fabrication of *in-situ* Nano PD-MMC by Friction Stir Processing (FSP) [10]. In this paper, a unique method of producing *in-situ* Nano porous PDC in solid state using FSP has been introduced. We report the evolution of *in-situ* Nano pores/cracks in PDC particles when SiCN cross-linked polymer was reinforced in copper metal matrix during multi-pass FSP. This method differs from the conventional methods used for producing porous ceramics and nobody has reported as per the author's knowledge. The pores developed in PDC particles have been micro structurally characterized in detail to understand the pore distribution and its morphology.

Experimental Procedure

A commercially available product, KDT Ceraset Polysilazane 20 (VL20) owned by Kion Corporation was used as the polymeric precursor for preparation of SiCN ceramics. The VL20 is a versatile liquid thermosetting resin. This polymer contains repeated units of silicon and nitrogen atoms which are bonded in an alternating sequence. The matrix material selected in the present study is pure copper (99.9%). SiCN cross linked polymer powder, having angular shaped particles with an average size of 10µm is used as reinforcement [10]. The powder is a cross-linked polymer having a density of ~1.0 gcm⁻³. Grooves (3 mm x 4 mm) were cut and holes (φ=3 mm) were drilled into a 6 mm thick copper plate and were filled with the above mentioned polymer powder. Four passes of FSP were carried out on a five-axis friction stir welding machine (BiSS - ITW, Bangalore) on the groove at a tool rotation speed of 1500 rpm and traverse speed of 25 mm/min. A frustum shaped threaded Densimet tool with shoulder diameter, pin diameter and pin length of 25 mm, 6 mm and 5 mm, respectively was used. A tool tilt angle of 3° was used. The processed plate was then pyrolysed at 800 °C in muffle furnace for 30 min to convert polymer into ceramic [10].

The samples were carefully polished using standard methods and ground with SiC abrasive papers through 3000 grit. Then the samples were polished with alumina slurry and finally with diamond paste using polishing machine. Ultrasonic cleaning was done for all samples to make the surface of the specimen free from dust/abrasive particles and preferably free of oxide layers. Samples were characterized using Scanning Electron Microscopy (SEM) (Sirion, Model VL 30FEG) with Energy Dispersive Spectroscopy (EDS) and Transmission Electron Microscopy (TEM, F-30).

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Results

Figure 1a shows the SEM micrograph of four multi-pass FSP of SiCN polymer reinforced Cu matrix composite at lower voltage i.e. 10 kV to avoid burning of polymer and Figure 1b shows the EDS elemental analysis of polymer reinforced composite. It has been observed that present elements are 27.26 wt% Cu, 32.48 wt% Si, 11.66 wt% C and 28.6 wt% O (was expected) in composite sample; nitrogen could not be analyzed by this method [10]. In the present work, the polymer powder is mixed with copper by FSP. The polymer powder is malleable and disintegrates into submicron size particles during multi-pass FSP (Figure 1a).

Figure 2a shows the SEM micrographs of FSP composite specimen with emphasis on PDC particle after pyrolysis at 800°C. It is observed that Nano-scale (~100 nm) pores are present in the PDC particles (Figure 2b) after pyrolysis due to the evolution of gases [10]. Micrographs were taken at higher magnification to confirm these pores for further investigation and it has been found that these were ~100 nm size pores (Figure 2c inset - marked by an arrow).

Energy-Dispersive-Spectroscopy (EDS) spot analysis was carried out on the PDC particle after pyrolysis (Figure 2d). The particle content shows 37.53 wt% Si, 25.95 wt% C, 33.88 wt% O and 2.65 wt% Cu. Nitrogen could not be analyzed by this method. Although

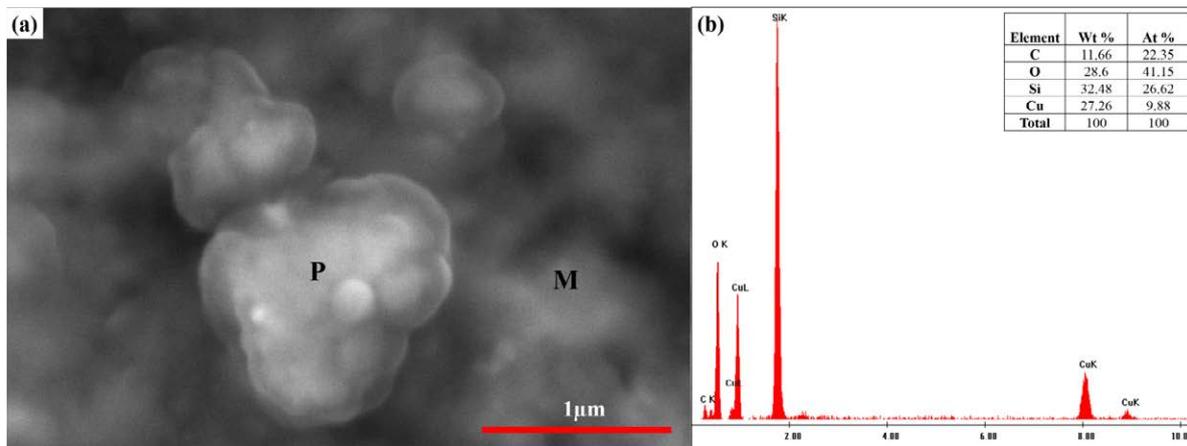


Figure 1: (a) shows the presence of SiCN (O) polymer particle (P) in Cu matrix (M) before pyrolysis (b) its elemental analysis.

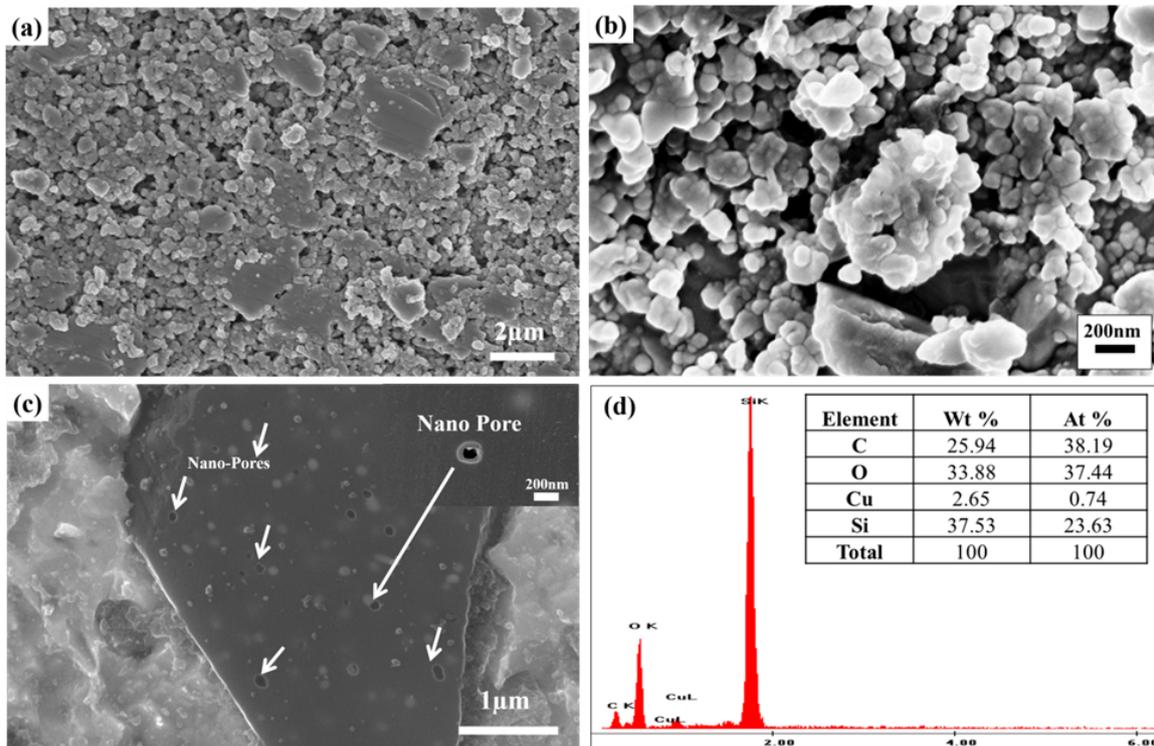


Figure 2: (a-b) shows the submicron pores in PDC particles marked after in-situ pyrolysis, (c) The nano-scale pores in PDC particles marked with arrows after pyrolysis (inset image) enlarge view and (d) its elemental analysis after pyrolysis.

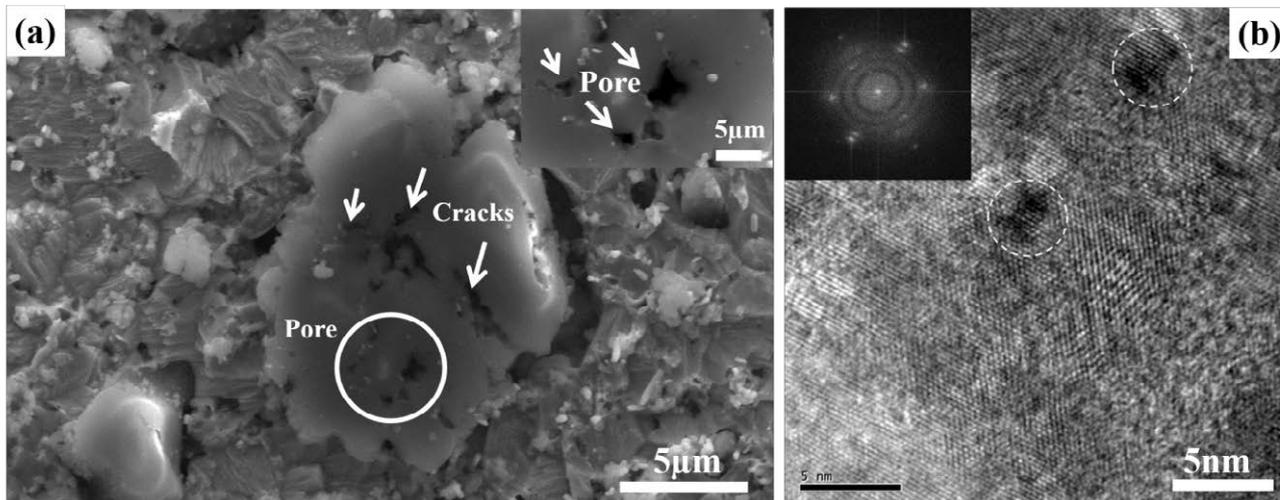


Figure 3: (a) Shows the submicron pores and cracks in PDC particles marked with arrows after pyrolysis (inset image) enlarged view, (b) Arrangement of the atomic planes of copper around a PDC particle (dark region) in PD-MMC by FSP (HR-TEM image).

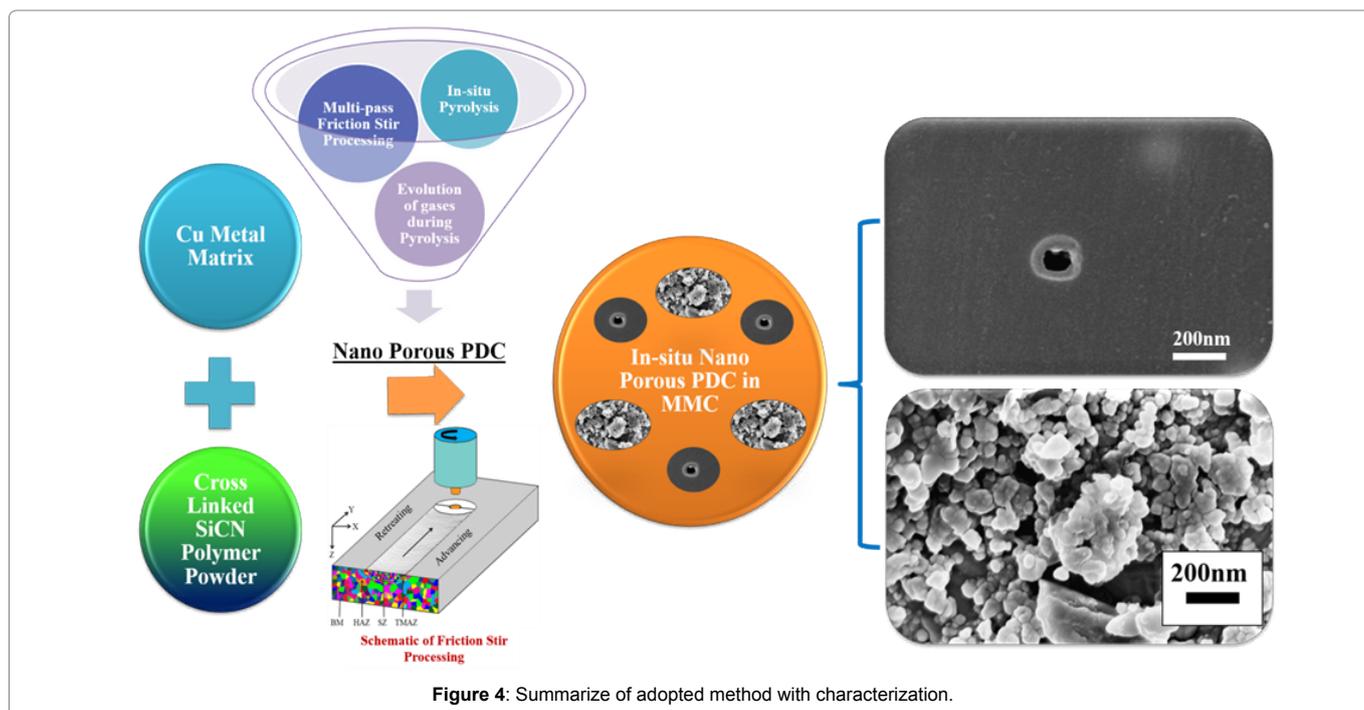


Figure 4: Summarize of adopted method with characterization.

the oxygen content can rise up to more than 10% if the precursor is exposed to air for prolonged periods [11]. The present composition shows even larger concentration of oxygen relative to nitrogen, suggesting the pickup of oxygen during external pyrolysis. Apart from Nano pores, cracks were also seen in the PDC particles after pyrolysis as shown in Figure 3a. These cracks are introduced due to sudden escape of gases upon pyrolysis.

Discussions

The evolution of volatiles (predominantly hydrogen and methane by breaking of C-H bonds) causes the formation of Nano pores in PDC particles. The polymer precursor inserts silicon, carbon and nitrogen (and, to some extent, oxygen) into the metal. Among these,

only silicon is a potential solid-solution strengthener [11] which forms ceramic residue before and after pyrolysis (Figure 1b and 2d). The most telling results of producing Nano pores are shown in Figure 2(a-c) where Nano pores are dispersed fully in PDC particles after pyrolysis. The pyrolysis of bulk FSP composite samples leads to high porous PDC material because of the formed volatile products.

As these pores are formed in PDC particles during fabrication of PD-MMC by FSP where PDC particles need to be dispersed at Nano scale but not possible due to the presence of clustered porous PDC particles. Here, FSP plays a crucial role and these pores are helpful to disperse the PDC particles at Nano scale because these porous PDC particles will have less fracture toughness (easily fractured) [10] and brittleness due to the predominant ionic or covalent nature of the

chemical bonding in ceramic compounds. These porous particles are easily fractured during further FSP and dispersed in the matrix at Nano scale with no pores in PDC particles [10]. FFT pattern of HR-TEM (Inset Image-Figure 3b) shows the polycrystalline ring pattern of Cu matrix and bright points of particles in the matrix. The calculated d-spacing of particle in the Cu matrix is 0.3nm which confirms the presence of PDC particle in the Cu matrix (d-spacing= 0.208 nm). Due to multi-pass FSP, open pores and voids are eliminated. This indicates that the proposed processing method can create tri-effects at one time i.e. forming *in-situ* Nano pores, avoiding significant agglomeration of the PDC particles and at the same time allows the uniform distribution of the ceramic particles in metal matrix. Figure 4 summarizes the work for better understanding.

Conclusion

This work indicated that the *in-situ* Nano porous PDC can be produced in metal matrix using FSP process and can be utilized further for Nano dispersion of PDC particles in the matrix homogeneously. The simplicity of this concept to produce *in-situ* Nano porous ceramics promise the widespread materials and mechanical applications such as producing metallic foams and porous metallic structures since organic precursors for several oxide and non-oxide ceramics are readily available for varies range of temperatures.

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