DEVELOPMENT OF INJECTABLE POLYMER-DERIVED CERAMICS FOR HIGH TEMPERATURE MEMS

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ABSTRACT

In this paper, a novel processing technique for fabrication of high temperature MEMS is reported. The process consists of four steps: (1) casting a liquid polymer precursor into molds with desired structures; (2) heating the filled mold for thermosetting the polymer; (3) bonding different solid polymer parts together using the same liquid polymer as an adhesive; (4) converting the polymer to a ceramic by thermal decomposition. The technology allows implementation of MEMS components with complex three-dimensional, multi-layer structures. The resultant polymer-derived ceramics, based-on amorphous alloys of silicon, carbon and nitrogen, can be used at temperatures up to 1500 ^{o}C.

INTRODUCTION

High temperature MEMS have received increased attention due to their many potential applications. For example, in some cases, microsystems need to operate in high temperature and harsh corrosive environments, such as sensors in gas engines. In other cases, the microdevices themselves contain high temperature environments, such as the microscale combustion chamber for a MEMS power source and a microscale turbine engine. The fabrication of high temperature MEMS is a two-fold problem: selecting high temperature materials and developing appropriate microfabrication techniques. Conventional MEMS components made with silicon bulk/surface-micromachining or LIGA-like techniques are not capable of long term operation at high temperatures because the structural materials (silicon in Si-micromachining, nickel or plastics in LIGA) can not survive at high temperature. Traditional ceramics can work at high temperature. However, their processing procedure is not compatible with available micropatterning techniques. Therefore, the development of new materials and appropriate microfabrication techniques for high temperature MEMS is of both scientific and practical interest to the MEMS community.

A technique under development for high temperature MEMS is chemical vapor deposition (CVD) of SiC [1]. CVD SiC is patterned using surface micromachining techniques. The disadvantage of this approach is that both CVD and SiC micromachining are difficult, time-consuming, complex and expensive procedures. Furthermore, it is difficult with this technique to fabricate three-dimensional components with high aspect ratios due to the planar nature of the CVD.

In this paper we report on novel injectable polymer-derived ceramics and appropriate micropatterning techniques associated with it for implementation of high temperature MEMS. This new technology is derived from the recently developed processing technique of polymer-derived ceramics, where bulk ceramics are fabricated by the thermal decomposition of compacted cross-linked polymer powder [2]. The ceramics thus obtained are amorphous alloys of silicon, carbon and nitrogen (SiCN) which remain amorphous and are thermally stable up to 1500 ^{o}C. The compositions of the new ceramics can be varied through using different polymer precursors (Figure 1), and can be tailored to produce SiCN with excellent thermal and mechanical properties.

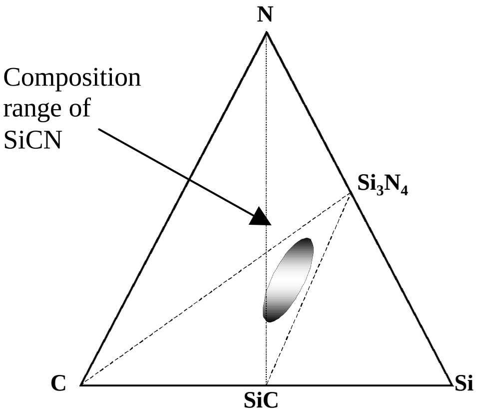


Figure 1. Phase diagram of silicon-carbon-nitrogen showing the compositions of SiCN.

Table 1 lists some physical properties of the SiCN, together with those of Si and SiC for comparison. The major properties of the SiCN are in the same range as those of SiC and superior over those of Si. The SiCN also shows creep resistance as good as SiC and Si_3N_4 [3, 4], while its oxidation resistance is even better than SiC and Si_3N_4 [5]. Obviously, the thermal shuck resistance appears very promising for SiCN. Thus SiCN ceramics are promising for high temperature applications. However, the SiCN obtained from polymer powder shows relatively low strength and hardness. This is believed to be due to the high porosity of powder derived ceramics (typically ~ 10 vol% porosity).

Table 1. Comparison of Physical Properties Between SiCN, Si and SiC.

	SiCN	Si	SiC
Density (g/cm^3)	2.20	2.33	3.17
E Modulus (GPa)	158	163	405
Poisson's Ratio	0.18	0.22	0.14
CTE (x 10^{-6}/K)	0.5	2.5	3.8
Hardness (GPa)	15	11.2	30
Strength (MPa)	250	175	418
Toughness (MPa.m$^{1/2}$)	3.5	0.9	4-6

INJECTABLE POLYMER-DERIVED CERAMICS

As already stated, polymer-derived ceramics using cross-linked powder as starting materials show low strength and hardness due to the high porosity. Furthermore, the powder route is not suitable for MEMS fabrication. In this section we describe a new processing technique for polymer-derived ceramics, casting process starting with liquid polymer precursors.

Casting process

Instead of using cross-linked polymer powder as starting materials, the new technique uses liquid polymer precursors to make bulk ceramics. The general procedure of the newly developed casting technique is schematically illustrated in Figure 2. First, a mold with desired features is fabricated using a variety of techniques, such as traditional machining, micromachining of silicon, and LIGA. A liquid phase polymer precursor is then cast into the mold. The mold and polymer precursor are heat-treated at ~ 250 ^oC for thermosetting the polymer. After thermal setting, the polymer becomes transparent solid which is easy to machine. Such solid polymer can then be separated from the mold if necessary. After thermal setting, the part is heat-treated at ~ 400 ^oC under isostatic pressure to cross-link the polymer. After this step, the polymer becomes infusible, remaining transparent. In the final stages the cross-linked polymer part is heat-treated at ~ 1000 ^oC to convert it to a monolithic ceramic part. The ceramics obtained from this procedure show the same nanostructure and compositions, and thus, possess similar properties as the polymer powder derived ceramics provided that the heat-treatment conditions are the same.

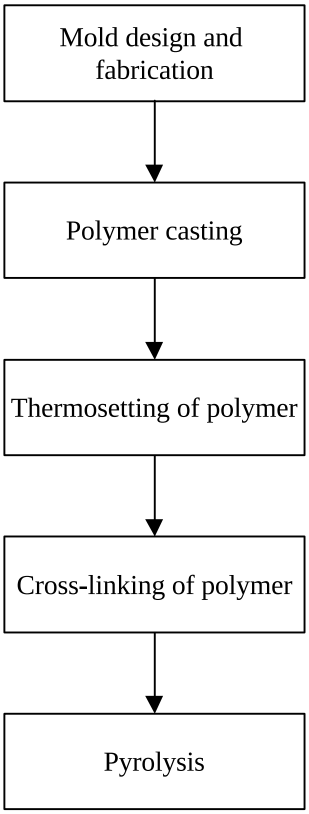
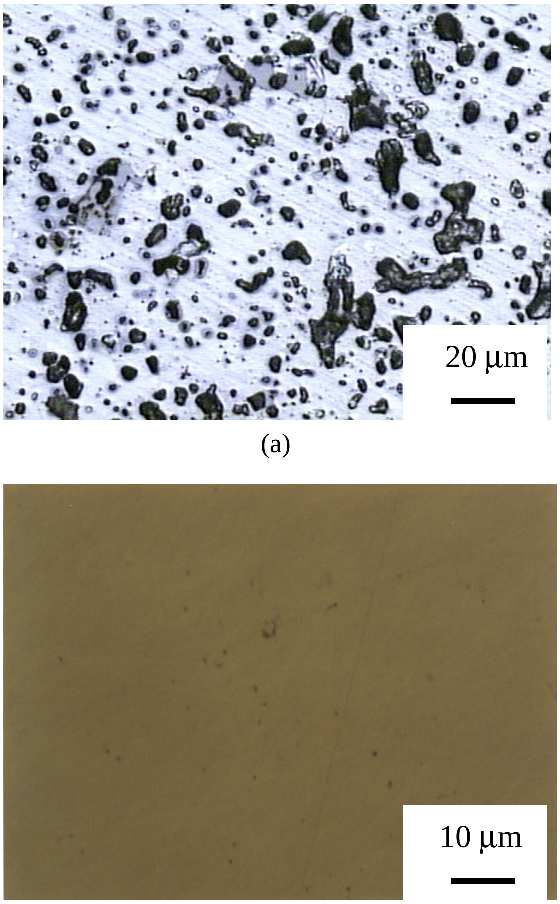


Figure 2. Illustration of process steps for injectable polymer-derived ceramics.

Figure 3 compares the SiCN microstructure for samples obtained by the powder route and the casting route technique. The improvement in microstructure is obvious. The sample from powder route shows high volume percentage of pores, while the casted sample shows very few observable pores or defects. The size of pores in the cased sample is also much smaller than that in the powder route sample. The last point is very important concerning MEMS applications. The scale of materials defects must be much less than that of the microstructures



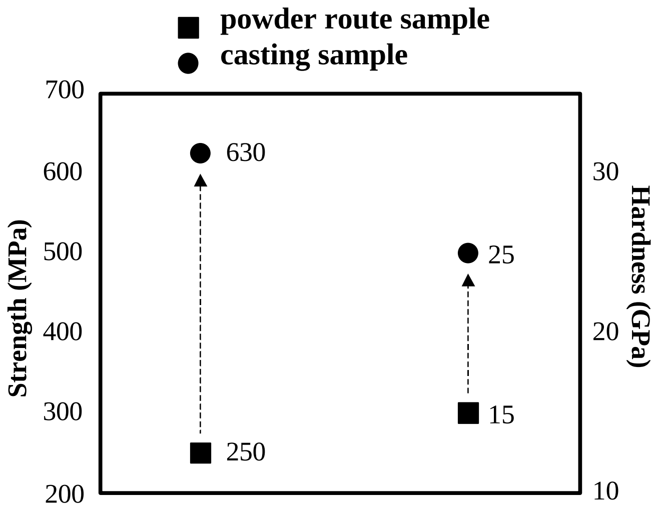
(a)

(b)

Figure 3. Scanning electron micrographs showing the microstructure of polymer-derived SiCN: (a) from powder route and (b) from casting route.

The key to the success of the casting route is the application of isostatic pressure during cross-linking step. The heat-treatment during cross-linking generates gaseous by-products. The out-going gases may cause forming and the formation of microcracks and disintegrate the sample [2]. In the casting approach, the applied isostatic pressure provides the obstacle to the nucleation of bubbles and microcracks. The gaseous by-products need to build up sufficient pressure to overcome the applied pressure before bubbles and microcracks can nuclei. Due to the rather open structure of the polymer, the gases will come out from sample by diffusion before they can build up high enough pressure (higher than the applied pressure). Thus, transparent and defect free cross-linked polymer can be obtained. The fact that no defects can be seen in the final ceramics indicates that the infusible polymer network has enough strength to survive during the further heat-treatment for thermal pyrolysis.

Figure 4 shows the strength and hardness of the SiCN from casting technique, together with that of the SiCN from powder route. The increase in both strength and hardness of casted materials as comparing with the powder derived materials is significant. Note that the density of casted sample is also higher than that of the powder derived sample, confirming the microstructural observation of Figure 3.



Density: 2.20 g/cm^3 (powder); 2.35 g/cm^3 (cast)

Figure 4. Comparison of strength and hardness of a powder-route sample and a casting-route sample.

Therefore, the new ceramic casting fabrication route substantially improves microstructure and mechanical properties of polymer-derived SiCN. Moreover, casting process is compatible with many available microfabrication techniques, including LIGA and bulk silicon micromachining.

Polymer-based bonding

The SiCN components derived from the casting process are single layer structures. Their shapes are limited due to the demolding requirements. However, "polymer-based-bonding" technique may be used for the fabrication of multi-layer structures. Experiments indicate that in order to obtain the best results, the bonding needs to be performed at the polymer thermal setting or cross-linking stages. The basic process is schematically shown in Figure 5. Figure 5 (a) shows two thermal set or cross-linked solid parts obtained using the procedure described in Figure 2. The same liquid polymer can then be pasted at the desired location as an adhesive layer, and the different pieces are then aligned and held together (figure 5 (b)). The assembled structure is first heat-treated for solidifying the adhesive layer, and then cross-linked under isostatic pressure (figure 5 (c)). Finally, the bonded structure is pyrolized for converting the polymer to ceramics (figure 5 d)).

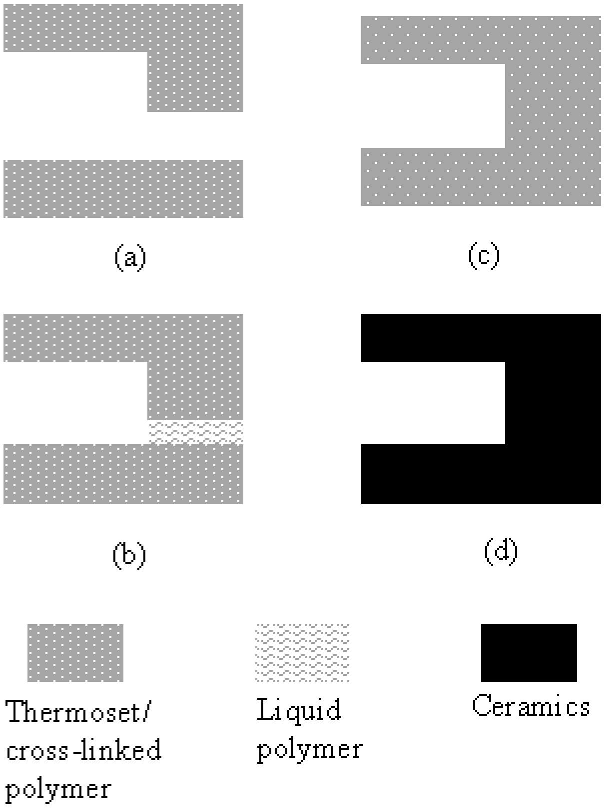


Figure 5. Illustration of process steps for polymer-based bonding of SiCN parts. (a) two solid polymer parts, (b) bonding parts together with a layer of liquid polymer, (c) cross-linked structure, and (d) ceramic multi-layer component.

The feasibility of the polymer-based bonding is also due to the liquid nature of the polymer precursor, which allows the atomic level contact at the interfaces between the adhesive layer and the solid polymer parts. Further heat-treatment at the temperature of thermosetting/cross-linking causes chemical reactions and establishment of the chemical bonds between the polymer in adhesive layer and the polymer in solid parts, reminiscent of the metal-based solder bonding process. Therefore, after cross-linking, the whole structure becomes one larger piece of polymer without noticeable interface. Such bonded structure behaves just like a single cast piece during further pyrolysis. This is consistent with the previous approach in which the cross-linked powder can be sintered together to form bulk ceramics [2].

Figure 6 shows a micrograph of two ceramic SiCN disks bonded together using the technique described in Figure 5. The bonding was performed on thermal set disks. Further examination indicated that there is no observable defect at bonding interface.

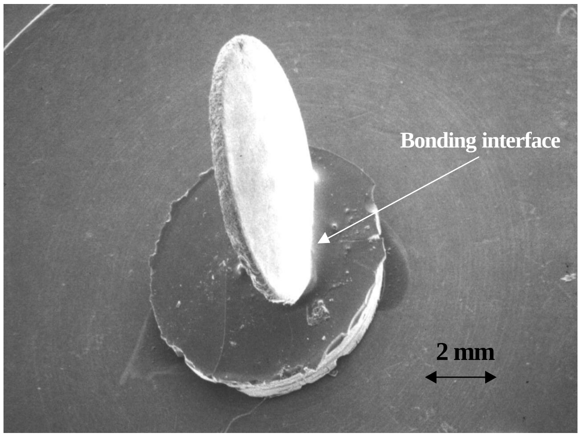
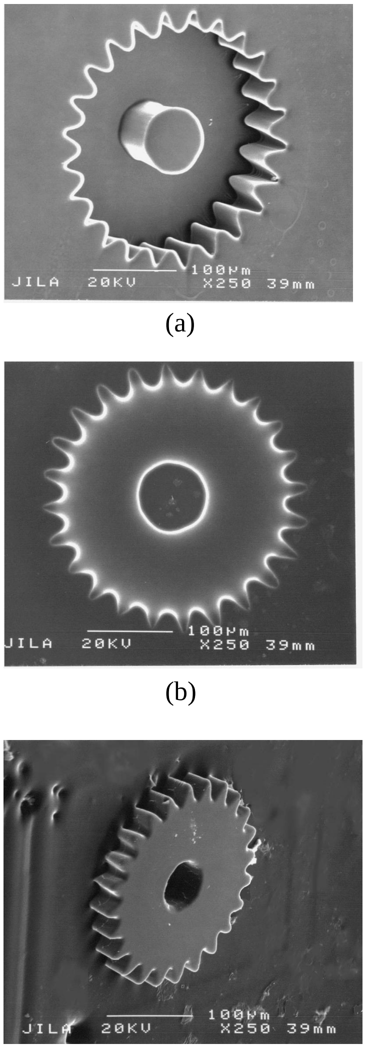


Figure 6. Two SiCN disks bonded together by the polymer-based bonding technique. Arrow indicates the bonding interface.

REPRESENTATIVE MEMS COMPONENTS

To demonstrate the feasibility of the new approach for the fabrication of MEMS, a SiCN micro-gear has been made using the injectable polymer-derived ceramics.

The casting mold is made from photoresist on a silicon wafer using lithographic techniques. The advantages of the photoresist mold include (1) simple fabrication procedures, and (2) the photoresist can be burned-out during pyrolysis, and thus no demolding is necessary. The mold is made from SU-8-25 photoresist, which allows fabrication of hih aspect ratio microstructures. The obtained photoresist mold for microgear is shown in Figure 7 (a). The liquid polymer precursor is then cast into the mold using the spin-on approach. Figure 7 (b) shows the SEM micrograph of the photoresist mold filled with polymer. The polymer filled mold is then thermally set, cross-linked and pyrolized following the procedure described in Figure 2. The obtained SiCN ceramic gear (200 μm diameter and 45 μm thickness with the hole of 80 μm diameter) is shown in Figure 7 (c). It can be seen that the SiCN gear replicates well the shape of the mold, demonstrating the excellent casting behavior of the liquid polymer. It is also important to note that there is approximately ~ 25 % linear shrinkage of the final ceramic gear as compared with the dimensions of mold.



(a)

(b)

(c)

Figure 7. (a) Photoresist mold, (b) the mold filled with polymer and (c) SiCN ceramic gear.

CONCLUSION

A novel injectable polymer-derived ceramics (SiCN) has been developed. The new materials exhibit excellent mechanical and thermal properties, very promising for high temperature applications. Furthermore, the new ceramic casting technique is suitable for the fabrication of MEMS components. A microscale SiCN gear has been made to demonstrate this technique. As compared to the existing MEMS materials and processes, the new technique substantially enhances the manufacturing capability for high temperature MEMS, as illustrated in Figure 8.

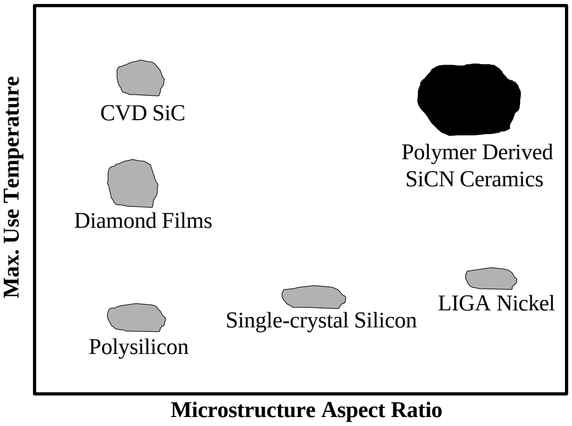


Figure 8. Diagram of micro-structure aspect ratio against maximum use temperature for different MEMS materials and processes.

ACKNOWLEDGEMENT

Work supported by the Defense Advanced Research Projects Agency (DARPA) and U.S. Air Force under contract # F30602-99-2-0543. Mr. Tsali Cross prepared Figure 6.

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