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1.5.4 Microstructure of SiC Ceramics Fabricated by Pyrolysis of Electron Beam Irradiated Polycarbomethylsilane Containing Precursors

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Abstract

A modified gel-casting method was developed to form the ceramics precursor matrix by using polycarbomethylsilane (PCMS) and SiC powder. The polymer precursor was mixed with SiC powder in toluene, and then the slurry samples were cast into designed shapes. The pre-ceramic samples were then irradiated by 2.0MeV electron beam generated by a Cockcroft-Walton type accelerator in He gas flow to about 15MGy. The cured samples were pyrolyzed and sintered into SiC ceramics at 1300°C in Ar gas. The modified gel-casting method leaves almost no internal stress in the pre-ceramic samples, and the electron beam curing not only diminished the amount of pyrolysis gaseous products but also enhanced the interface binding of the polymer converted SiC and the grains of SiC powder. Optical microscope, AFM and SEM detected no visible internal or surface cracks in the final SiC ceramics matrix. A maximum value of 122 MPa of flexural strength of the final SiC ceramics was achieved.

Keywords: SiC ceramics, electron beam, ceramic precursor, polycarbomethylsilane,

1. Introduction

Silicon carbide (SiC) ceramics and SiC based ceramic composite possess various extraordinary properties [1] such as high temperature resistance (SiC dissociates at 2815°C), high hardness, high physical strength, low expansion factor and low neutron activation cross section, good resistance to corrosion by other materials. These outstanding properties make it possible to be widely used in extreme environment such as the first wall material of fusion reactor, turbine engine nozzles etc. Nevertheless, high quality SiC ceramics is very difficult to be fabricated through traditional ways.

Generally, conventional methods to fabricate SiC ceramics can be classified into 2 categories: 1) Using fine SiC powder and firing agent such as Al_2O_3 to form bonded ceramics at high temperature 1800~2200°C [2], traditional gel casting [3] technique belongs to this category; 2) Physically and/or chemically deposit SiC in molecular or atomic level to form

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bulk ceramics, such as chemical vapor deposition (CVD) method [4]. The first way is easy to produce in large scale, but the products properties are very limited, and high temperature firing facilities is needed. Furthermore, this method cannot be used to fabricate SiC_f/SiC composite as the SiC fiber decomposed at temperature higher than 1600°C [5]. The second way can produce high strength SiC ceramics, but takes long time to form even a small SiC bulk sample; Furthermore, expensive facilities have to be adopted.

In present paper, we used a modified gel-casting method to form the ceramics precursor matrix by using polycarbomethylsilane (PCMS) and SiC powder, followed by electron beam (EB) curing, to fabricate high quality SiC ceramics at lower sintering temperature (1300°C). The present modified gel-casting method leave almost no internal stresses in the precursor samples. Internal stress and volume shrinking are the two major reasons, which cause the formation of cracks in the final SiC ceramics matrix.

2. Experimental

2.1 Materials

Polycarbomethylsilane (PCMS), $[-Si(CH_3)HCH_2-]_n$, electronic grade, average Mw. is 800, m.p. 79~84°C, was purchased from Aldrich Chemical Company. Silicon carbide powder was purchased from Showa Denko Company; the grain size is about 4×10^2nm. Toluene and other chemical reagents used in experiments are all analytical pure grade.

2.2 Sample preparation and analysis

PCMS, SiC powder and toluene were mixed into slurry and degassed in a hybrid mixer. Then the slurry was casted into selected shapes, slowly dried in vacuum to remove residual toluene. After that the samples were irradiated in He gas flow to about 15MGy by 2.0MeV EB generated by a Cockcroft-Walton type accelerator. After quenching at 500°C, the cured samples were pyrolyzed and sintered into SiC ceramics at 1300°C in Ar gas.

The physical strength was measured by using an Instron 4302 type comprehensive mechanical property analyzer. The microstructure of the SiC ceramics was observed by using Keyence VH-6300 type CCD optical microscope, SPA400 type Atomic Force Microscope (AFM) and JSM-5600 type Scanning Electron Beam Microscope (SEM). Gel content was measured through solvent extraction [7] by using toluene.

3. Results and Discussion

3.1 Function of electron beam curing

Polymer precursor pyrolysis has been very successful in fabricating SiC ceramics fibers [6, 7], as well as infiltration of sintered porous ceramics to further density [8]. However, in recent years, reports [9] on polymer converted bulk SiC ceramics showed that it's very difficult to avoid the formation of surface and internal cracks mainly caused by the volume shrinkage, which occurred in the conversion process of polymer to ceramics.

Through high-energy radiation especially EB curing, SiC fibers have been successfully

fabricated by using polymer precursors [6~7]. The polycarbosilane (PCS) precursor used for synthesis of SiC fiber, after cured by electron beam to 12~15 MGy, will not form detectable cracks or bubbles. TGA and GC-FTIR analysis results [7] confirmed that CH_4, H_2 and other low molecular weight gaseous compound evolved out in both processes of EB irradiation and pyrolysis. The EB curing effectively diminished the pyrolysis gaseous production; moreover, 3-dimensional crosslinked infusible and insoluble gel was generated by EB irradiation, and the precursor's fibrous shape was reserved in the conversion process of polymer to ceramics.

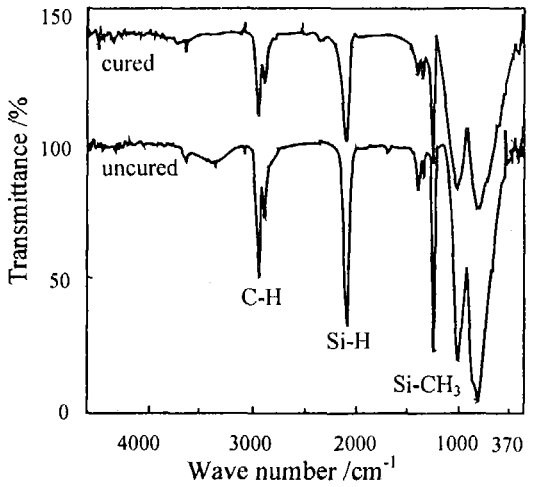

Fig.1 FTIR spectrogram of uncured PCMS and the 15MGy electron beam cured one.

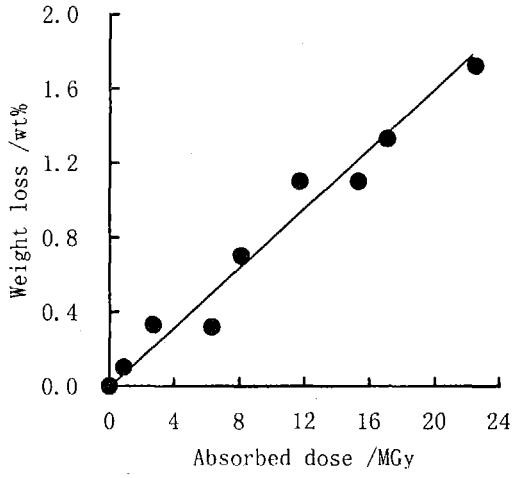

Fig. 2 Percent weight loss of PCMS after irradiated to various absorbed dose

However, PCS was not selected as precursor of SiC in this paper, because of its high brittleness at ambient temperature; it was very difficult to form bulk precursor samples of this polymer with enough mechanical strength.

The newly selected SiC ceramics precursor, PCMS, can also be effectively cured by EB. As shown in **Fig.1**, the strong and sharp FTIR peaks at 2105cm^{-1} caused by Si-H stretching, decreased after the sample was cured by 15MGy (gel content was about 75wt%); synchronously, the absorbance in 760～670cm^{-1} (Si-CH_2) increased, which indicates that -Si-CH_2-Si- type crosslinking bond was formed, mainly by the reaction of Si-H group, similar to the radiation curing mechanism of PCS [7].

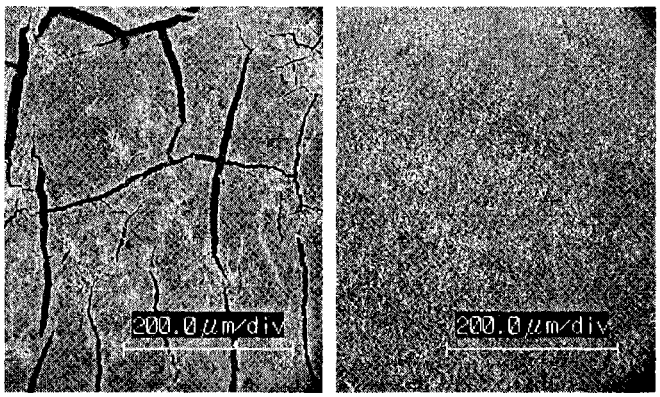

Fig.3 Optical Microscope surface image of SiC ceramics sintered from a) un-cured and b) EB cured precursors

The weight loss of PCMS, caused by the release of gaseous products, increased almost linearly within the experimental range of absorbed dose (**Fig.2**). Uncured precursors, either PCS or PCMS, generated large amount of gaseous products, and many bubbles as well as

cracks were detected in the bulk samples (**Fig.3a**). The cured PCMS bulk samples, after pyrolyzed and sintered, no cracks were observed as shown in **Fig.3b**.

3.2 Microstructure of the SiC ceramics

Only inorganic materials including SiC powder and binders such as alumina were used in traditional fabricating method [1] to minimize shrinkage during firing of the pre-ceramic part. Typically, the gel casting process [3] for forming ceramics, which was very successful in making complex-shaped automotive parts such as turbines, also sinters only inorganic powders at a high temperature of about 1800°C. These reported methods use inorganic binders or firing agent, which melt at high temperature forming glass phase, to "bind" SiC powder. As the traditional firing agent has poorer high temperature resistant properties than SiC, the application of these SiC ceramics is limited.

The PCMS converted SiC was used as binder to join the SiC powder together in this paper. EB curing possesses the well known advantage that crosslinking could be achieved without extra curing agent or any other chemicals; makes it possible to fabricate SiC ceramics with high purity and excellent high temperature resistant properties.

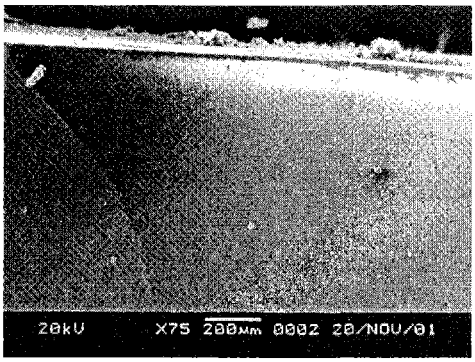

Fig.4 Cross-section SEM image of the SiC ceramics sintered from EB cured sample

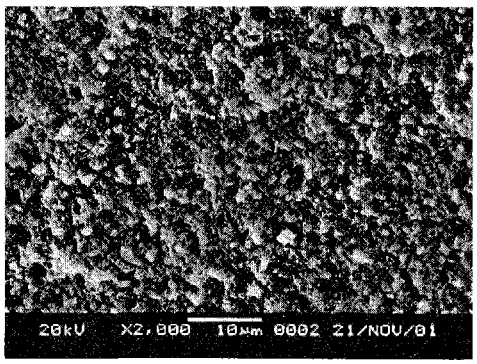

Fig.5 Highly amplified cross-section SEM image of the SiC ceramics sintered from EB cured samples

SiC ceramics sintered from 15MGy-cured PCMS containing precursor samples shows very good surface and internal structure integrity (**Fig.3~5**). The solid grains of SiC powders were well jointed by the PCS converted SiC as shown in **Fig.6**.

However, in the non-cured precursor samples, after pyrolyzed and sintered in Ar gas, some cracks were observed by optical microscope (**Fig.3**). As the density of SiC (**Tab.1**) is at least 2 times that of the polymer precursor, volume shrinking is unavoidable after PCMS is converted to SiC ceramics. The EB curing generated infusible gels, as well as diminished the gas evolution, "fixed" the solid structure of the polymer containing precursor samples. After pyrolyzed and sintered, PCMS was converted into

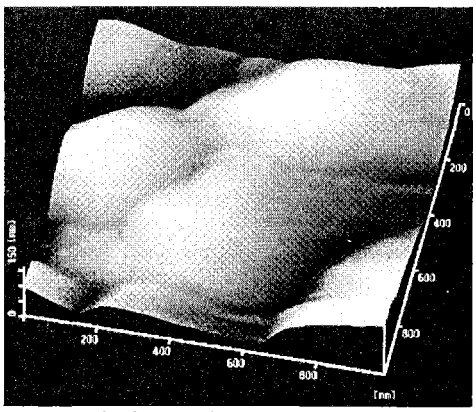

Fig.6 Atomic force microscope image of the SiC ceramics cross-section

SiC, and leaves "micro-porous" ceramics.

The PCMS converted SiC joined very well with the inorganic SiC powder as demonstrated by the AFM image shown in **Fig.6**. Whereas, some lacuna still existed in the samples, which might be caused by the non-uniform distribution of the polymers in the pre-ceramic samples. The micro-pores in the PCMS converted SiC area should be very small, as they were formed mainly by release of H_2 and CH_4 from the infusible EB cured precursor samples, and are not visible to presently used means.

3.3 Physical properties of the SiC ceramics

The modulus of SiC ceramics sintered from EB cured samples (7.1×10^4 MPa) is slightly higher than that of the non-cured (6.4×10^4 MPa). On the flexural strength of SiC ceramics, EB curing almost doubles the 3-point bending strength, as shown in **Fig.7**.

Compared to traditionally bonded SiC ceramics, the EB cured one possesses satisfactory physical strength, as shown in **Tab.1**. Similar value of 3-point bending strength to the composite bonded SiC ceramics was achieved at present.

Composite bonded SiC ceramics is a relatively new grade of product formed by slip casting. It uses high purity fine grain SiC powder, blended with elemental silicon and a binder system. It is formed into shapes via slip casting and is sintered in a controlled nitrogen atmosphere at temperatures exceeding 1400°C. Composite bonded silicon carbide has relatively high strength among conventional SiC ceramics products.

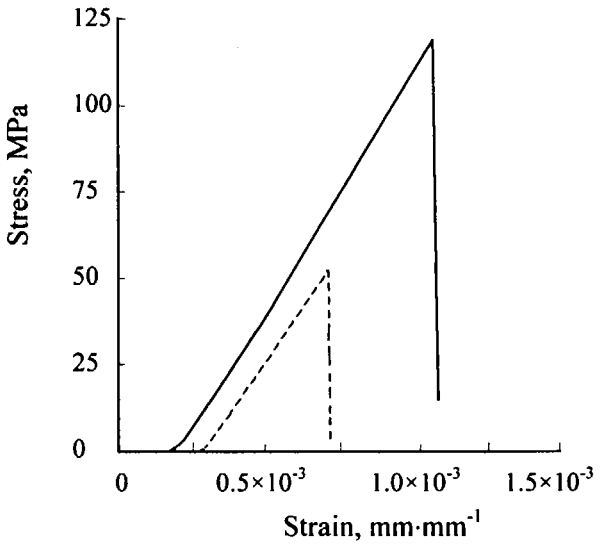

Fig.7 Effect of EB curing on the stress-strain properties of SiC ceramics (— EB cured, ····· direct fired)

Table 1. Physical properties of several SiC ceramics fabricated by bonding methods*

Product	Bulk Density ($g\cdot cm^{-3}$)	Porosity (%)	3-point bending strength (MPa)
Clay Bonded SiC	2.2-2.5	13-28	23
Nitride Bonded SiC	2.4-2.7	16	45-65.5
Oxy/Nitride Bonded SiC	2.2-2.4	18	41
Composite Bonded SiC	2.5-2.6	16	130
Present paper's SiC	2.3	~24	122

* Properties of other bonded SiC ceramics were selected from ref. [10].

Nitride bonded silicon carbide is commonly produced using a mixture of silicon carbide powder and finely divided elemental silicon, and sintered in a nitrogen atmosphere at high

temperature. Beginning at approximately 1100°C, the nitrogen gas and silicon metal react forming silicon nitride, or Si_3N_4, to bond the SiC powder together. If it is sintered in a controlled nitrogen and oxygen atmosphere, then oxy/nitride-bonded silicon carbide could be produced, which has slightly higher porosity, lower density and performance in wear applications. Clay bonded silicon carbide is normally formed via static pressing of a mixture of silicon carbide powder and clay, and the bond is formed during sintering where the clay softens and forms a glassy phase.

4. Conclusion

High quality SiC ceramics could be fabricated by using PCMS ceramics precursor and EB curing. The major effect of curing is: 1) To decrease the amount of gaseous pyrolysis products, and minimize volume shrinking in the process of polymer to ceramics; 2) To enhance the interface binding between polymer converted SiC and the SiC powder. The properties of SiC ceramic in present paper could be further improved by optimizing the distribution of PCMS in the precursor samples, the ratio of PCMS and SiC powder, and by using nano-sized SiC powder. As low firing temperature (1300°C) was adopted, the present result will be the basis for high quality SiC_f/SiC ceramics matrix composite (CMC) fabrication.

The presently achieved physical properties as shown in **Tab.1** are high enough to produce high-quality and complex-shaped fine ceramic parts such as gears used in high temperature wear application area. The point is that, using PCMS converted SiC as the binder, the resulted SiC engineering ceramics does not contain any high Z elements such as Al (formed from Al_2O_3 binder); this can decrease the neutron activation cross-section. The high temperature resistant property and the resistance to corrosion by other materials will also be better than conventional products,

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