

[Article ID] 1003 - 6326(2000)06 - 0783 - 05

Application of zirconium in preparation of polycarbosilane derived ceramics^①

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[Abstract] The metallic zirconium (Zr) powder as active filler was applied in polycarbosilane (PCS) preceramic precursor derived ceramics. It was found that the addition of Zr decreases the porosity of the green compact and, since Zr can react with N₂ to produce nitride, the ceramic productivity is increased. The ceramic productivity will be 100 % when the volume fraction of Zr/PCS is 44 %. Zr also enhances the three-point bending strength of the ceramic with the strength of 104 MPa when the volume fraction of Zr/PCS is 60 %. However, the addition of Zr in PCS can not restrain the linear shrinkage upon pyrolysis, the linear shrinkage increases with increasing the volume fraction of Zr/PCS. Phase composition was analyzed using X-ray diffraction (XRD). Fracture surfaces of the specimens after three-point bending tests were examined on the scanning electron microscope (SEM).

[Key words] active filler; zirconium (Zr); polycarbosilane (PCS); ceramics

[CLC number] TB323

[Document code] A

1 INTRODUCTION

Manufacturing of ceramic materials from preceramic organosilicon polymers has recently attained increasing interest because of highly attractive shaping properties and low fabrication temperatures. Polycarbosilane (PCS), polysilazane (PSZ) and polysiloxane can be used to prepare novel ceramic materials, such as ceramic fibers, coating, and matrix for ceramic composites^[1,2].

The basic limitation to make a monolithic ceramic from polymer precursors is the extraordinary high volume shrinkage and pronounced porosity accompany with the mass loss of the small molecules of the polymer during pyrolysis. When the polymer in conversion can not be relaxed through viscous flow or diffusion, extensive cracking and pore will destroy the integrity of the material. Thus, direct conversion of a polymer compact to a dense ceramic is almost impossible^[3~5]. Two methods were proposed to solve the drawbacks. First, synthesizing new precursors with high ceramic productivities to decrease the porosity and shrinkage. The other way is addition of inert and (or) active filler powders in the polymer precursor. The inert powders, such as SiC do not react with the polymer during pyrolysis, simply occupy space to reduce the effective volume of the voids and increase the overall density of the pyrolyzed product. The active filler powders which react with the decomposition products of the polymer or a reactive gas molecule

during the pyrolysis will expand to compensate the polymer shrinkage and a near-net-shape conversion can be achieved. An additional advantage of the powders is that they may help prevent the development of cracks through the material. Therefore, adding active filler was an effective method to solve the drawbacks mentioned above^[4~6].

Seyferth and Greil^[3~6] studied the Ti, Cr, Cr-Si₂, and MoSi₂-controlled polysiloxane, polycarbosilane, and polysilazane pyrolysis. Tobias^[7] reported the structure development on Ti-controlled polysiloxane pyrolysis. Sung^[8] investigated the procedure of Ti-controlled polysiloxane pyrolysis in various atmosphere. ZHOU^[9] studied the influence of Ti on the porosity and pore size in the similar system.

The application of zirconium (Zr) in the polycarbosilane (PCS) precursor to prepare SiC ceramic is studied in the present paper. The chemical reactions, the microstructure of resulted ceramics, as well as the influence of Zr content on the shrinkage, ceramic productivity, and mechanical properties, are investigated.

2 EXPERIMENTAL

2.1 Raw materials

The raw materials used and their specifications were listed in Table 1.

2.2 Experimental procedure

① [Foundation item] Project (59682009) supported by the National Natural Science of China

[Received date] 1999 - 09 - 06; [Accepted date] 2000 - 01 - 25

Table 1 Raw materials and their specifications

Raw material	Molecular formula	Specification	Density/($\text{g}\cdot\text{cm}^{-3}$)	Characteristic
Polycarbosilane	$[\text{SiHCH}_3\text{CH}_2]_n$	Brown solid	1.15	Softening point: $\sim 210^\circ\text{C}$
Silicon carbide	SiC	Gray powder	3.20	$< 2.5\ \mu\text{m}$
Zirconium	Zr	Black powder	6.52	$< 38\ \mu\text{m}$
Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	Colorless liquid	0.86	AR

The SiC powders with the mean diameter $2.5\ \mu\text{m}$ and (or) the Zr powder $< 38\ \mu\text{m}$ were dispersed in the PCS-xylene solution for 8 h by ultrasonic vibration followed by evaporation of the solvent through vacuum. The well-dispersed solid was ground and sieved to small particles, which were then molded by 25 MPa pressure at room temperature. The green compacts were thus prepared. The green compacts were pyrolyzed in a tube furnace under a flowing nitrogen stream up to $1\ 000^\circ\text{C}$ in three steps program with average rate of $1^\circ\text{C}/\text{min}$ followed by holding for 1 h.

Densities of the green compacts and the resulted ceramics were measured according to Ref.[10]. The linear shrinkage was defined as the ratio of the difference between the size of the resulted ceramics and that of the green compact to the size of the green compact. Phase composition was determined by X-ray diffraction (XRD) using CuK_α radiation with a nickel filter. Flexural strength were measured by three-point bending test (30 mm) with rectangular bars ($3\ \text{mm} \times 4\ \text{mm} \times 35\ \text{mm}$) that were surface finished by diamond polishing. Fracture surfaces of the specimens after three-point bending tests were examined on the scanning electron microscope (SEM). The processing scheme was summarized in Fig.1.

3 RESULTS AND DISCUSSION

3.1 Influence of Zr content on density of green compacts

The PCS content was invariable in the paper, namely, the mass ratio between PCS and the green compact was 15 % (in mass)^[11]. The Zr content was defined according to the volume ratio between Zr and PCS, Zr/PCS, which was chosen as 10 %, 20 %, ... or 60 %. The corresponding green compact and the resulted ceramics was named as Z10, Z20, ... or Z60, respectively. To have a comparison, the green compact in which the Zr was excluded (named as Z0) was also investigated. The influence of Zr contents on the densities and linear shrinkage of the green compacts and their pyrolysis products and mechanical properties of the resulted ceramics were investigated. The influence of the Zr/PCS on the density of the green compacts is shown in Fig.2. The results were compared with the calculated porosity.

Here the theory density ρ_h was calculated according to

$$\rho_h = \sum \rho \varphi$$

where the ρ and φ are the density and volume fraction of each composition, respectively. The calculated porosity P was defined as

$$P = (\rho_h - \rho) / \rho_h$$

where ρ is the real density of the green compact.

Ideally, when Zr content increased, the theory density of the green compacts increased since the density of Zr ($\rho_{\text{Zr}} = 6.52\ \text{g}\cdot\text{cm}^{-3}$) is higher than that of SiC ($\rho_{\text{SiC}} = 3.2\ \text{g}\cdot\text{cm}^{-3}$). From Fig.2, the real density of the green compacts increase with higher Zr content, and the calculated porosity decreases with increasing the Zr content, which can be explained as that the small SiC powders and viscous PCS could fill in the pores among Zr powders. When the volume ratio of Zr/PCS is higher than 50 %, the calculated porosity decreases slowly since the pore is near saturation.

3.2 Influence of Zr content on linear shrinkage of resulted ceramics

The green compacts were pyrolyzed up to $1\ 000^\circ\text{C}$ under a nitrogen stream in a tube furnace to prepare the ceramics. The influence of Zr content on the linear shrinkage of the resulted ceramics was investigated through measuring the size of the green compacts and their pyrolysis products. The results are shown in Fig.3.

From Fig.3, when the Zr content increased, the linear shrinkage of the resulted ceramics increases too. The reason might be explained as the following three aspects.

First, while the temperature rises, the volume shrinkage of PCS happens, therefore the pores form, the shrinkage of the green compacts take place naturally. The shrinkage increases with increasing the Zr content for much more pores formed.

Secondly, the reaction activities between Zr and the gas volatile, free carbon, and nitrogen during pyrolysis of PCS, respectively, are low. The reactions can't begin until the pyrolysis of PCS is almost completed. The volume expansion after the reactions can not restrain the shrinkage for the formation of the ceramic frame.

Last, the volume effects after the reactions are also low. The volume expansions of the reactions between Zr and the gas volatile, free carbon, and nitrogen are -21 %, +9 %, and +3 %, respectively^[2,4].

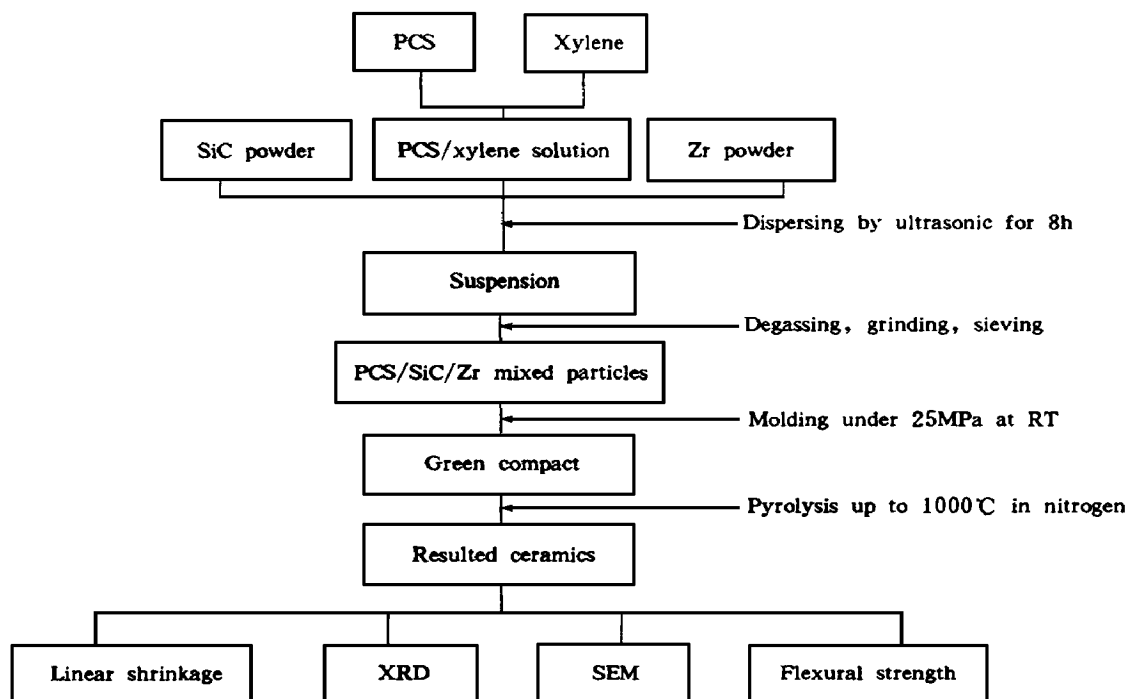


Fig.1 Flow chart of processing PCS/SiC/Zr mixture and reaction pyrolysis

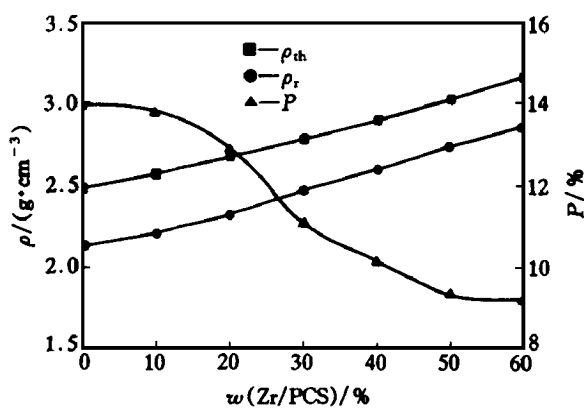


Fig.2 Influences of Zr content on density and calculated porosity of green compacts

ρ_{th} —Theoretical density; ρ_r —Real density; P—Porosity

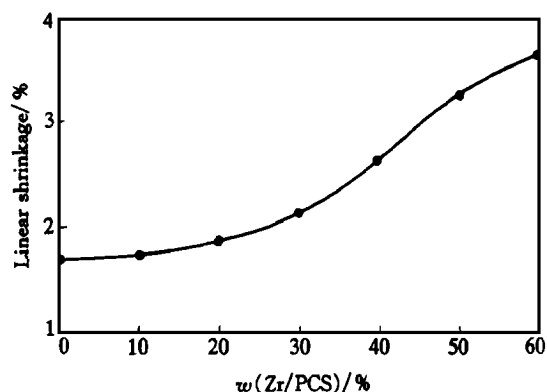


Fig.3 Influence of Zr content on linear shrinkage of resulted ceramics

Therefore, the near-net-shape conversion of PCS-ceramics could not be achieved through adding Zr in PCS.

3.3 Influence of Zr content on density and ceramic productivity of resulted ceramics

The densities of the resulted ceramics were measured by the method reported by Erik^[10], while the ceramic productivity was obtained from the mass ratio of the green compact and the resulted ceramics. Presume the mass of PCS in the green compact is m_p , that of the green compact is m_g , and that of the resulted ceramics is m_c , therefore the ceramic productivity (r_{cp}) is calculated by the following, $r_{cp} = (m_c - m_g + m_p) \cdot 100\% / m_p$. The influence of Zr content on the density and ceramic productivity of the resulted ceramics is shown in Fig. 4.

As shown in Fig. 4, the density and ceramic productivity of the resulted ceramics generally increased when the Zr content increased for a series of reactions involving Zr with N_2 and gas volatile of PCS occurred during the pyrolysis process. The higher density can be explained as that the main products of Zr, ZrN, have a higher density ($\rho_{ZrN} = 7.32 \text{ g} \cdot \text{cm}^{-3}$). The higher ceramic productivity caused by Zr can easily be understood as the introduction of non-volatile Zr and the resulted compounds. It was easy to find that the ceramic productivity would be 100% when the volume ratio of Zr/PCS was 44% from Fig. 4. It could be improved from the XRD pattern of Z60 (Fig. 5). To have a contrast, that of Z0 was shown at the same time.

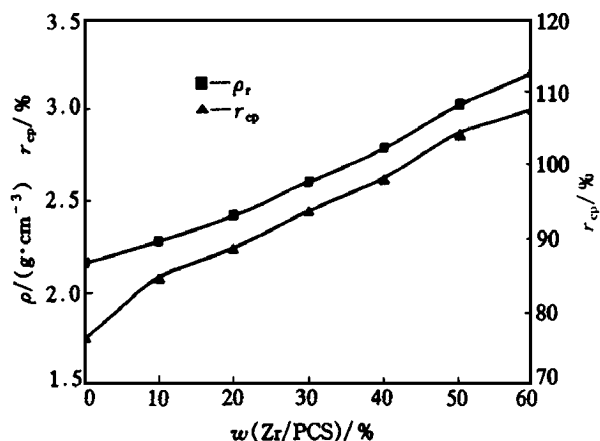


Fig.4 Influences of Zr content on density and ceramic productivity of resulted ceramics

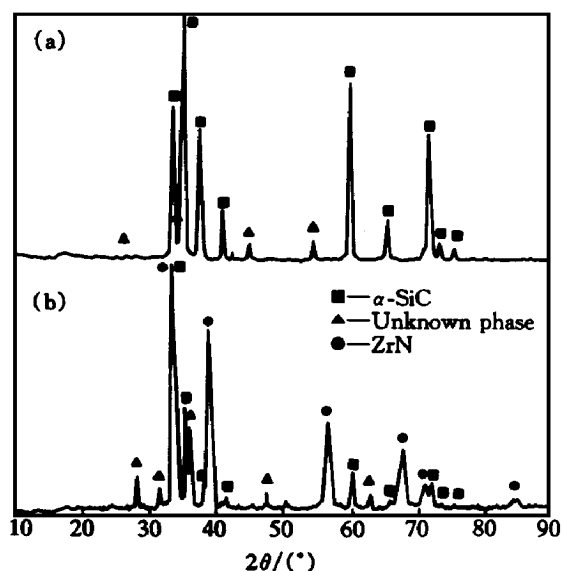
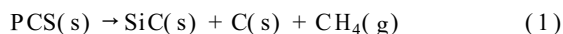
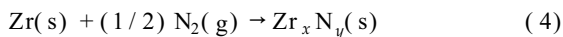
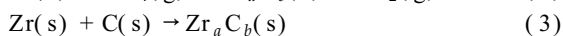
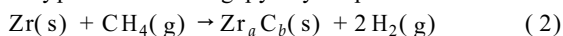


Fig.5 XRD patterns of pyrolysis products
(a) —Z0 ; (b) —Z60

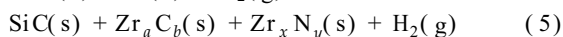
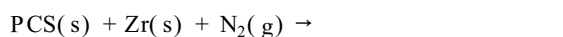
Therefore, if C(s) was denoted as free carbon, CH₄(g) as gas volatile of PCS during pyrolysis, the pyrolysis reaction of PCS could be described simply as the follows:



However, when active filler Zr was added in PCS, a series of reactions take place with various reaction byproducts during pyrolysis process



The total reaction would be



where Zr_aC_b and Zr_xN_y means the stoichiometric and nonstoichiometric compounds between Zr and C and N, respectively. From Fig.5, the final product of Zr after copyrolysis is ZrN. Furthermore, some active filler can react with PCS derived SiC to form a

new compound phase, lead to new volume effect.

3.4 Influence of Zr content on mechanical properties of resulted ceramics

Two advantages of adding active filler in the precursor are expected. First, as mentioned above, the ceramic productivity of the precursor increases while the shrinkage decreases upon pyrolysis. Secondly, the mechanical properties of the resulted ceramics, such as three-point bending strength, could also be significantly improved. The influence of Zr content on the three-point bending strength of the resulted ceramics is listed in Table 2.

Table 2 Influence of Zr content on three-point bending strength of resulted ceramics

Specimen	w(Zr/PCS) / %	ρ* / (g·cm ⁻³)	Flexural strength / MPa
Z0	0	2.16	63.8 ± 2.25
Z10	10	2.28	80.7 ± 4.50
Z20	20	2.42	82.9 ± 2.76
Z30	30	2.60	87.0 ± 3.93
Z40	40	2.78	91.8 ± 13.3
Z50	50	3.02	99.3 ± 16.1
Z60	60	3.20	104 ± 10.6

* —In green compacts; ** —Density of pyrolysis product

The strength of Z60 reached 104 MPa, which is 1.6 times of that of Z0. The essential effect of the Zr fillers could be explained into three aspects. First, they act as crack-stoppers through the reactions forming C and N containing products to prevent the development of cracks through the composites. Secondly, the density of the resulted ceramics increases by introducing Zr, therefore, the porosity decreases. The third, the porosity distribution and the microstructure of resulted ceramics are improved, which can be proved from the SEM observation of the resulted ceramics. Fig.6(a) shows the fracture surface of Z0 (without Zr) with a loose bonding between powders, irregular pore shape and poor pore distribution. These features tend to form stress concentration leading to a low flexural strength. As comparison, the fracture surface of Z60, shown in Fig.6(b), demonstrates close bonding of the powders, therefore, the stress concentration could be eliminated and result in a high flexural strength. However, long cracks also exists in the matrix. The reason might be the following two. One is the coefficient of thermal expansion (CTE) mismatch between nitride ($7.9 \times 10^{-6} \text{ K}^{-1}$) and(or) carbide ($6.7 \times 10^{-6} \text{ K}^{-1}$) of Zr and the SiC matrix ($4.8 \times 10^{-6} \text{ K}^{-1}$). Cracks would form while the temperature decreases after pyrolysis. The other is that, as mentioned above, the reaction activities between Zr and the gas volatile, free carbon, and nitrogen during pyrolysis of PCS, are relatively low. The reaction would not begin until the pyrolysis of

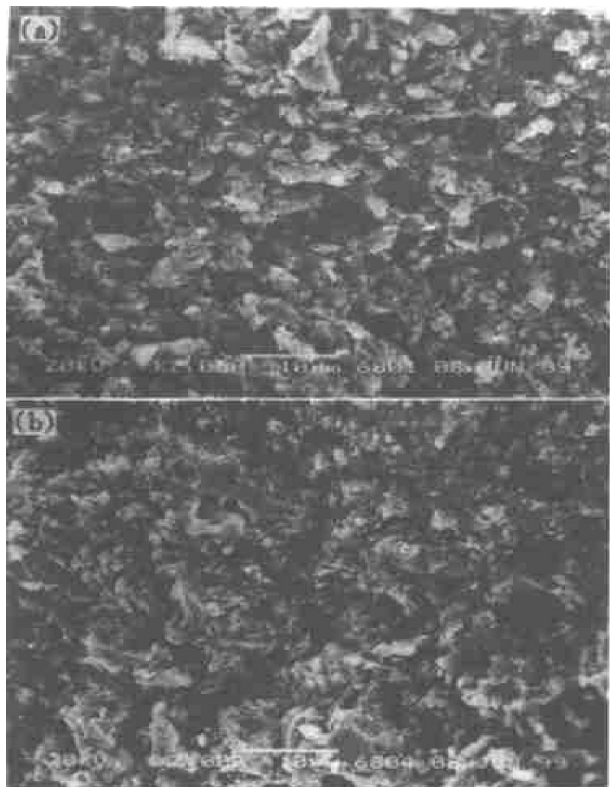


Fig.6 SEM fractographs of pyrolysis products
(a) —Z0 ; (b) —Z60

PCS is almost complete. The basically formed ceramic frame would be destroyed because of the volume expansion after the reactions. So the cracks formed, and the flexural strength of Z60 is not high. To decrease the cracks and improve the strength of resulted ceramics, suitable temperature ramp should be chosen.

3 CONCLUSIONS

1) The active filler Zr in PCS-SiC composites can increase the density of the green compact. The higher the Zr content is, the lower the porosity of the green compact will be.

2) The Zr filler increases the shrinkage of the green compact after pyrolysis. The higher the Zr content is, the larger the linear shrinkage will be.

3) The Zr filler can increase the ceramic productivity of PCS. The ceramic productivity will be 100 % while the volume ratio of Zr/PCS is 44 %.

4) The Zr filler can enhance the three-point bending strength of the ceramics with the strength of 104 MPa when the volume ratio of Zr/PCS is 60 %.

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(Edited by HUANG Jin song)