

## Carbide Ceramics from Active-Filler-Controlled Pyrolysis in CH<sub>4</sub> Atmosphere

Keon-Taek Kang, Deug-Joong Kim, Annette Kaindl,\* Peter Greil\*

*SungKyunKwan University, Department of Materials Engineering, Suwon, Korea*

*\*University of Erlangen-Nuernberg, Department of Material Science, Erlangen, Germany*

(Received November 17, 1999)

**Abstract** The formation, microstructure and properties of novel ceramic composite materials manufactured by active-filler-controlled polymer pyrolysis were investigated. In the presence of active filler particles such as transition metals, bulk components of various geometry could be fabricated from siliconorganic polymer. Molybdenum- and tungsten-filled polymer suspensions were prepared and their conversion to ceramic composites by annealing in CH<sub>4</sub> atmosphere were studied. Dimensional change, porosity and phase distribution (filler network) were analyzed and correlated to the resulting hardness values. Molybdenum and tungsten as active filler were carburized completely to Mo<sub>2</sub>C, W<sub>2</sub>C and WC in CH<sub>4</sub> atmosphere. Consequently, microcrystalline composites with the filler reaction products embedded in a silicon oxycarbide glass matrix were formed. Hardness was increased with increasing carburization and reached 8.6-9.5 GPa in the specimen pyrolyzed in CH<sub>4</sub> atmosphere.

### Introduction

Novel ceramic composites can be obtained by pyrolysis from preceramic polymer/active filler mixtures.<sup>1-3)</sup> This processing route has some important advantages with respect to conventional sintering techniques. The reaction temperatures are lower (<1500 °C) than those required for normal sintering, and plastic shaping technologies, such as extrusion and injection molding, are available for the fabrication of composite ceramics with complex geometry. Moreover, the volume increase during the reaction of the active filler with decomposition products of the polymer or reaction gas atmosphere compensates the polymer shrinkage, therefore, near net shape ceramics with low shrinkage can be achieved.<sup>4)</sup>

Polysiloxane (RSiO<sub>1.5</sub> with R=H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>3</sub>, etc.) is a relatively inexpensive polymeric precursor produced on an industrial scale and has a high ceramic yield up to 85 wt%.<sup>5)</sup> Using polysiloxane as preceramic polymer, an amorphous silicon oxycarbide phase is formed above 800 °C. The microstructure of the resulting ceramic composite from polymer/active filler system consists of carbide and

nitride which is embedded in the polymer derived Si-O-C matrix.<sup>3,6)</sup> Transition metal carbides such as TiC, WC, Mo<sub>2</sub>C, TaC are prominent as reinforcing compounds in an oxycarbide matrix due to the extremely high melting point, excellent high temperature strength and high hardness.

In the previous work,<sup>7,8)</sup> novel ceramic hard materials were developed by using Mo and W as active filler which were dispersed in polymethylsiloxane. Ceramic composites with less than 5% porosity could be obtained by reaction pyrolysis between 1000-1500 °C under nitrogen atmosphere. However, the carbon content in the polymethylsiloxane/active filler mixtures was not sufficient to carburize all the active filler materials, therefore, unreacted Mo and W still remained in the specimens after pyrolysis. In the present work, a CH<sub>4</sub> atmosphere as additional carbon source was used during pyrolysis. Subsequently, the resultant microstructures and properties of novel ceramic hard materials were investigated.

### Experimental Procedure

A commercially available polysiloxane was chosen

as ceramic precursor. Polymethylsiloxane, NH2100 (Chemische Werke Nuennchritz, Germany), is characterized by a molecular composition of (CH<sub>3</sub>-SiO<sub>1.5</sub>)<sub>n</sub> with average molecular mass of 22,862 g/mol. Molybdenum with a grain size of 2-4 μm (Chemper, Karlsruhe, Germany) and tungsten with a grain size of 1.08 μm (Korea Tungsten Co, Daegu, Korea) were used as active fillers.

Polymer (60 vol%) and filler (40 vol%) were mixed with acetone and homogenized with mechanical and ultrasonic stirring. After removal of solvent with a rotavapor, the mixtures were dried at 120 °C and were broken up to make a powder. The mixtures were warm-pressed in a metal die with an axial pressure of 30 MPa at 230 °C for 30 min.

The pyrolysis was performed in an electrically heated tube furnace in CH<sub>4</sub> atmosphere at a pressure of 0.1 MPa. The typical heating cycle involved heating up to 550 °C at the rate of 5 °C/min, holding at this temperature for 4 hr, a second ramp at the rate of 1-2 °C/min up to final temperature of 1000-1500 °C with a 4 hr hold and final cooling at the rate of 5 °C/min.

The density and open porosity of the ceramic products were measured by the water immersion technique. Total porosity was estimated from the theoretical density which was assumed from the density measurement by a helium pycnometer (Accu Pyk. 1330, Micromeritics, Duesseldorf, Germany) on samples after milling. Shrinkage was calculated from the measurement of dimensional change during pyrolysis. Phases were identified by X-ray diffraction using a Cu K<sub>α</sub> radiation and microstructures were examined by SEM. An image analyzer (Image Pro-Plus, Media Cybernetics, MD, USA) was used to characterize microstructures. Hardness were measured by using a Vickers indentation with indentation load of 98 N.

## Results and Discussion

Figures 1 and 2 show the XRD patterns of Mo- and W-filled specimens pyrolyzed in N<sub>2</sub> and CH<sub>4</sub>, respectively. From the figures, it can be observed

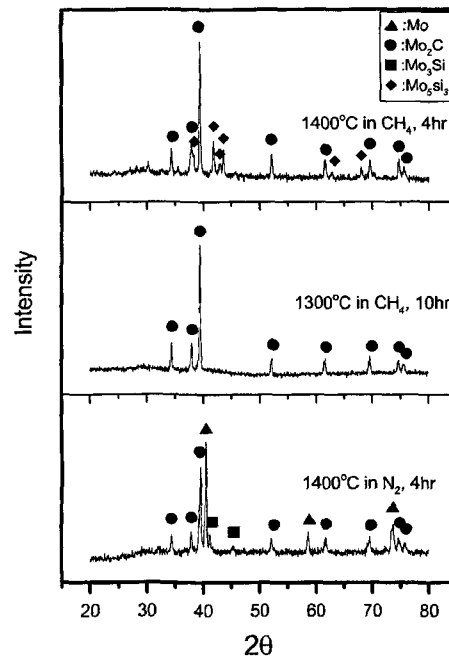


Fig. 1. XRD-spectrum of Mo-filled specimens pyrolyzed at different temperatures in N<sub>2</sub> and CH<sub>4</sub> atmosphere.

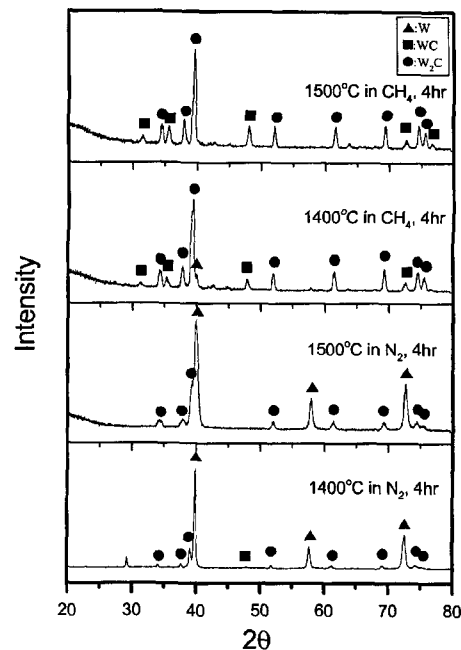


Fig. 2. XRD-spectrum of W-filled specimens pyrolyzed at different temperatures in N<sub>2</sub> and CH<sub>4</sub> atmosphere.

that the peak intensity of carbide in CH<sub>4</sub> atmosphere was higher than that in N<sub>2</sub> atmosphere.

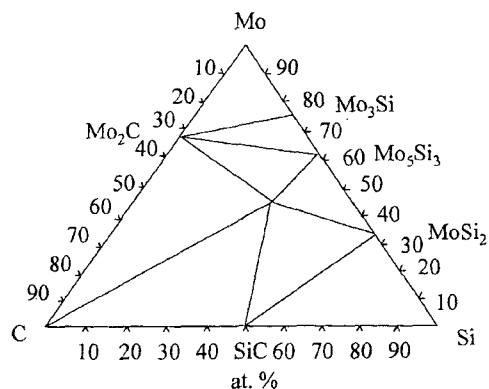


Fig. 3. Ternary phase diagram of the system Mo-Si-C at 1327 °C(9).

This suggests that the formation of carbide phases was favoured in  $\text{CH}_4$  atmosphere. In the case of Mo-filled specimens (Fig. 1), small peaks of  $\text{Mo}_3\text{Si}$  appeared in  $\text{N}_2$  atmosphere at 1400 °C. On the other hand, the formation of  $\text{Mo}_5\text{Si}_3$  occurred in  $\text{CH}_4$  atmosphere at the same temperature.

According to Si-Mo-C phase diagram (Fig. 3)<sup>9</sup>, with increasing carbon content the system moves to compositions with preferred  $\text{Mo}_5\text{Si}_3$  formation instead of  $\text{Mo}_3\text{Si}$ . The formation of  $\text{Mo}_5\text{Si}_3$  has also been reported from polysiloxane-, polysilazane- and polycarbosilane/filler mixtures<sup>7, 10</sup>. Due to the increase of carbon content from  $\text{CH}_4$  atmosphere, it is believed that the formation of  $\text{Mo}_5\text{Si}_3$  is favoured. When the specimen was pyrolyzed at 1300 °C for 10 hr, the carburization of Mo was completed and residual Mo was not found based on the XRD data.

In the case of W-filled specimens (Fig. 2), the formation of tungsten silicide was retarded up to 1500 °C because of the higher formation energy of tungsten silicides than those of molybdenum silicides.<sup>11</sup> Above 1400 °C in  $\text{N}_2$ ,  $\text{W}_2\text{C}$  became a major phase and residual W was still found. Tungsten is in equilibrium with WC at the temperature below 1300 °C, and with  $\text{W}_2\text{C}$  at the higher temperature in the tungsten side of the W-C phase diagram (Fig. 4)<sup>12</sup>. In methane atmosphere, the equilibrium moves to the two phase region of WC- $\text{W}_2\text{C}$ . The residual W reacts with  $\text{CH}_4$ , yielding completely WC and  $\text{W}_2\text{C}$  carbide phases

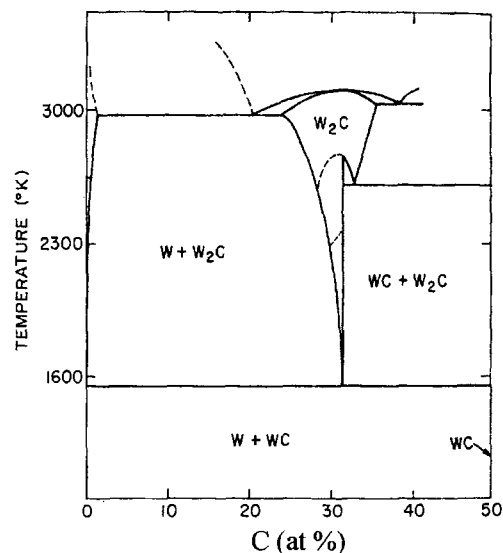


Fig. 4. Tungsten side of the W-C phase diagram(12).

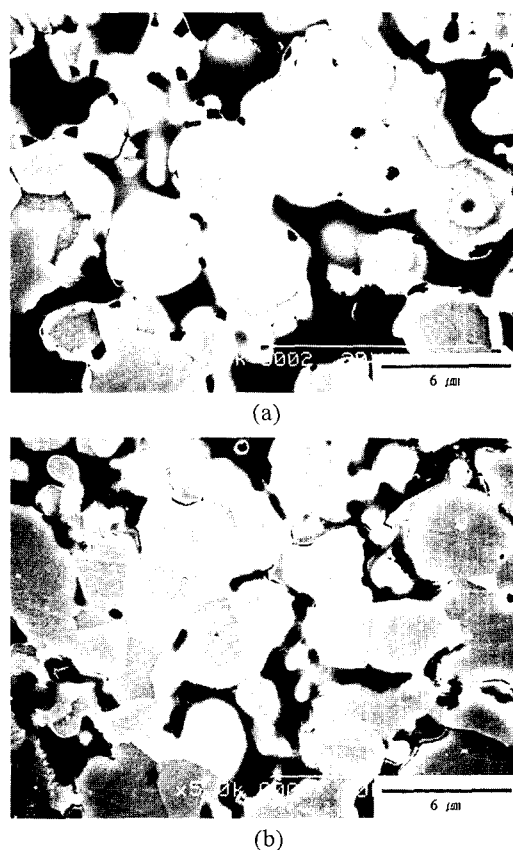


Fig. 5. Microstructures of Mo-filled specimens pyrolyzed (a) at 1400 °C for 4 hr in  $\text{N}_2$  atmosphere and (b) at 1300 °C for 10 hr in  $\text{CH}_4$  atmosphere.

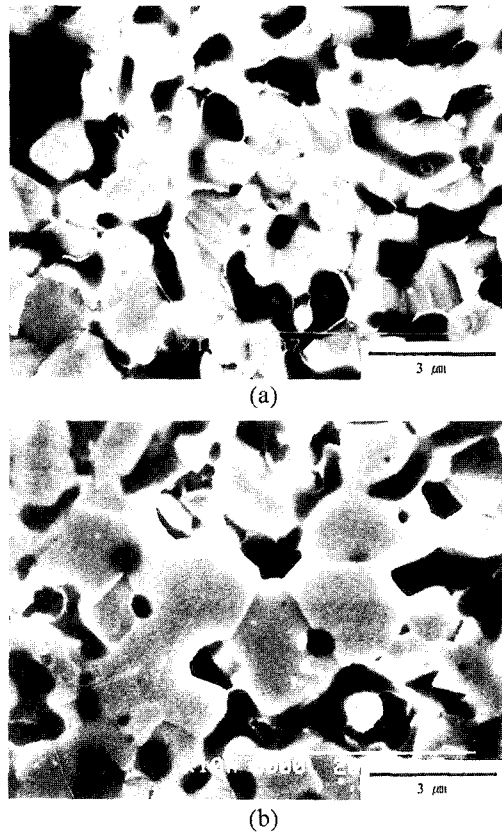


Fig. 6. Microstructures of W-filled specimens pyrolyzed (a) at 1500 °C for 4 hr in N<sub>2</sub> atmosphere and (b) at 1500 °C for 4 hr in CH<sub>4</sub> atmosphere.

at 1500 °C in CH<sub>4</sub> atmosphere.

Figures 5 and 6 show the etched microstructure of specimens pyrolyzed in N<sub>2</sub> and CH<sub>4</sub>. Pores

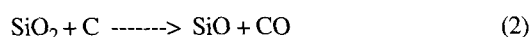
were frequently found at boundary between filler particle and matrix. Darker phases were considered to be silicon oxycarbide phase whereas light phases consisted of unreacted metal or carbide particles. Silicon oxycarbide matrix phases derived from polysiloxane above 800 °C have been reported in a number of works.<sup>3,13</sup> It is to be noted that core-shell microstructures, especially in the Mo-filled specimen (Fig.5-a), indicated surface controlled carburization reaction between filler and matrix, producing a shell of carbide on each metal particle. As the reaction proceeds, the carbide phase on the surface continues to grow in thickness until all of the metal has been consumed. Faceted carbide grains were predominant in the microstructures of specimens from CH<sub>4</sub> atmosphere.

Some properties of polymer derived ceramic composites via active filler controlled pyrolysis are summarized in Table 1. Most of specimens still contained 3-5 % total porosities after pyrolysis, even if the open porosities were transformed into a closed porosities, resulting in less than 0.5 % open porosities. In the case of Mo-filled specimen pyrolyzed at 1400 °C in CH<sub>4</sub>, a remarkable increase of porosity was found. The stability of the silicon oxycarbide glass is known to be dependent on the composition of the glass. Silicon oxycarbide glass with high carbon content tends to decompose and can form a new generation of porosity due to the release of CO and SiO.<sup>14</sup> The silicide formation and carbothermal reduction

Table 1. Results of specimens reacted at various conditions

Specimen	Density (g/cm <sup>3</sup> )	Open Porosity (%)	Total Porosity (%)	Shrinkage (%)	Fraction of solid particle* (vol%)	Hardness (GPa)
Mo 1400°C, 4 hr, N <sub>2</sub>	7.07	0.32	2.5	11.3	57.06	7.8
Mo 1300°C, 10 hr, N <sub>2</sub>	6.45	0.25	4.2	11.2	59.29	8.6
Mo 1400°C, 4 hr, CH <sub>4</sub>	6.51	6.32	10.1	9.39	63.83	5.8
W 1400°C, 4 hr, N <sub>2</sub>	12.17	0.55	4.8	12.12	49.76	7.3
W 1500°C, 4 hr, N <sub>2</sub>	12.32	0.22	4.3	13.07	56.83	8.8
W 1500°C, 4 hr, CH <sub>4</sub>	12.37	0.42	3.7	9.2	60.73	9.5

due to increased instability of silicon oxycarbide glass is expected to be enhanced formation of gaseous species and results in the increase of porosities within the specimen pyrolyzed at 1400 °C in CH<sub>4</sub>, as following possible reactions (1) and (2).



The volume fraction of solid particles, which was measured by image analyzer from microstructures, was increased slightly by increasing the carburization of Mo and W.

The mechanical properties were strongly influenced by the phase changes and porosities developed during pyrolysis.<sup>7,8)</sup> Hardness was increased by 10 % with increasing carburization in CH<sub>4</sub> and reached 8.6 and 9.5 GPa in the specimens filled with Mo and W, respectively. The hardness of ceramics strongly depends on the fraction of residual porosities. With increasing porosity, the hardness decreases exponentially.<sup>15)</sup> The hardness of 14.8 GPa at zero porosity was estimated from using the rule of mixture with the values of volume fraction in Table 1. For the estimation, the hardness of Si-O-C glass of 7 GPa<sup>14)</sup> and the hardness of carbide phases of 20 GPa<sup>16)</sup> were used. The specimens produced by the active-filler-controlled reaction process still contain about 4 % of residual porosities. This indicates a further potential for increasing hardness with decreasing porosity.

### Conclusion

Ceramic composites with less than 5 % porosity were obtained through the incorporation of reactive Mo and W powders in preceramic poly-methylsiloxane with the subsequent pyrolysis in a reactive gas atmosphere. Molybdenum and tungsten as active filler were completely carburized to Mo<sub>2</sub>C and W<sub>2</sub>C/WC in CH<sub>4</sub> atmosphere, respec-

tively. Consequently, microcrystalline composites with the carbide reaction product embedded in a silicon oxycarbide matrix were formed. Hardness was increased with increasing carburization and reached 8.6-9.5 GPa in the specimen pyrolyzed in CH<sub>4</sub> atmosphere.

### Acknowledgement

The Korea-German Cooperative Science Program supported this project. Korea Science & Engineering Foundation (KOSEF) and German Science Foundation (DFG) are gratefully acknowledged.

### References

1. P. Greil and M. Seibold, in Ceramic Transactions vol. 19, Advanced Composite Materials, Ed. by M.D. Sacks, Am. Ceram. Soc., OH, 1991, 43.
2. P. Greil, M. Seibold, T. Ery, Mater. Res. Soc. Symp. Proc., **274** (1992), 155.
3. T. Ery, M. Seibold, O. Jarchow, P. Greil, J. Am. Ceram. Soc., **76** (1993), 207.
4. P. Greil, J. Am. Ceram. Soc., **78** (1995), 835-848.
5. P. Greil and M. Seibold, J. of Mat. Sci., **27** (1992) 1053.
6. M. Seibold and P. Greil, J. Eur. Ceram. Soc., **11** (1993) 105.
7. A. Kaindl, W. Lehner, P. Greil and Deug J. Kim, Mat. Sci. & Eng., **A260** (1999) 101.
8. K. T. Kang, Deug J. Kim and P. Greil, J. of the Korean Ceramic Soc., **35** (1998) 939.
9. G. S. Upadhyaya, Nature and Properties of Refractory Carbide, Nova Sci. Publ., NY, 1996, 192.
10. D. Seyferth, N. Bryson, D.P. Workman and C. A. Sobon, J. Am. Ceram. Soc., **74** (1991) 2677.
11. Ihsan Barin, Thermochemical Data of Pure Substances, VCH, Weinheim, 1989.
12. D. K. Gupta, L. L. Seigle, Met. Trans. 6A, **11** (1975) 1939.
13. G. R. Renlund, S. Prochazka and R. H. Doremus, J. Mater. Res., **6** (1991), 2716.
14. G. R. Renlund, S. Prochazka and R. H. Doremus, J. Mater. Res., **6** (1991) 2723.
15. I. J. McColm, Ceramic Hardness. Plenum, NY, 1990.
16. R. Kieffer and F. Benesovsky, Hartstoffe, Springer Verlag, Wien, 1963.