

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CERAMIC MATRIX COMPOSITES (CMCs) FROM POLYSILOXANE AND INERT / ACTIVE FILLERS

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ABSTRACT

Active and inert filler incorporated ceramic monolithic composites were developed based on the pyrolytic conversion of poly(phenyl)siloxane and poly(methyl)siloxane. Also, the thermal transformation of the polymers was monitored under various pyrolysis temperatures (900-1500°C). The results showed that formation of amorphous silicon oxycarbide (SiO_xC_y) ceramics occurred at temperatures below 1300°C, however, at higher temperatures (~1500°C) crystalline β-SiC phases formed. CMC monoliths were prepared by mixing preceramic polymers with inert (SiC) and active (Ti) particulate fillers. Active fillers were used to compensate the mass losses by reaction of active filler and decomposition products of the polysiloxanes. Curing of the green bodies took place under hot press (15 MPa, 200°C). During pyrolysis at 900-1500°C under inert atmosphere, cross-linked green compacts of the particulate/polymer systems were converted into ceramic bodies. The effect of the precursor and the filler type, filler concentration and pyrolysis temperature on the microstructure, phase development, mass losses, densification and mechanical behavior of composites were investigated. X-ray diffraction (XRD), infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) coupled with EDX analyzer were used for microstructural characterization of the products. Vickers indentation tests were performed for evaluating the mechanical behavior of the CMCs.

1. INTRODUCTION

Fabrication of ceramic matrix composites (CMCs) from pyrolytic conversion of preceramic polymers has gained considerable attention in recent years due to their unique combination of low temperature processing, applicability of versatile plastic shaping technologies and microstructural control capabilities [1]. In addition, low manufacturing temperatures allow low cost processes and the preparation of metastable phases. Poly(silanes), -(carbosilanes), -(silazanes) and -(siloxanes) have been the most studied precursors because of their commercial availability and high ceramic yields. Silicon oxycarbide glasses that contain silicon atoms bonded to oxygen and carbon randomly are a group of materials that can be produced by pyrolysis of preceramic precursors. The replacement of part of the divalent oxygen atoms of silica by tetravalent carbon atoms leads to an improvement in the thermomechanical properties [1-4]. Substitution of oxygen in silica glass with carbon is not feasible through conventional glass melting techniques due to their high processing temperatures (1600-1800°C), however, it may be obtained via pyrolysis of preceramic polymers [2]. Main drawback of the polymer pyrolysis technique is the manufacturing of crack free bulk ceramic components. Due to inherent density increase by outgassing of the organic matter, extensive shrinkage that causes the formation of pores and cracks may occur. To compensate this effect and to control shrinkage and crack formation, a relatively new concept, active filler controlled polymer pyrolysis process (AFCOP) has been developed [5-7]. In this approach, polymer matrix is loaded with active fillers such as, B, Si, Ti, CrSi₂, MoSi₂; that reacts with the decomposition products of the polymer (CH₄, C₂H₄, C₆H₆ etc.) to form new phases; carbides, nitrides or oxides and undergo a volume expansion. The volumetric expansion from the filler phase reaction may compensate the shrinkage and increase ceramic yield upon pyrolytic decomposition of the polymer.

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The objective of the present study is to develop ceramic composites from the pyrolysis of two preceramic polymers; poly(phenyl)siloxane and poly(methyl)siloxane with the addition of the active (Ti) and inert (SiC) fillers. Also, the effects of polymer and filler type, filler concentration and pyrolysis temperature on the microstructure, phase development, densification, mass losses and hardness values were investigated. Furthermore, the pyrolytic conversion of the both polymers was monitored. Thermal transformation under inert atmosphere was monitored at pyrolysis temperatures between 900-1500°C. The products of the pyrolysis process were analyzed using X-ray diffraction (XRD), infrared analysis (FTIR), and scanning electron microscopy (SEM) coupled with EDX analyzer.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Sample Preparation

Commercially available poly(phenyl)siloxane (PPS) (H62C, Wacker Chemie, GE) and poly(methyl)siloxane (PMS) (MK, Wacker-Belsil, GE) was used as preceramic polymers. As inert filler, SiC with particle sizes in the range of 10-40 μm , and active filler, Ti with particle size of -149 μm were used.

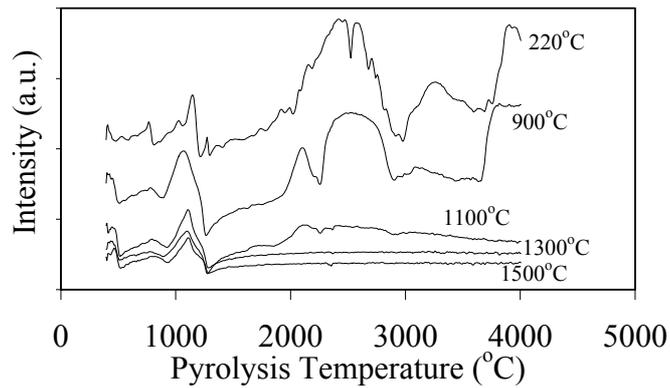
To monitor the thermal transformation of the preceramic polymers neat polymers without any filler addition were prepared. Neat PPS was used as received and PMS, a solid solvent free silicon resin, was dissolved in toluene and mixed with Zr-acetylacetonate, which was used for cross-linking. Polymers were vacuumed for half an hour and casted in Teflon moulds and cured in an oven at 220°C under open-air atmosphere. Pyrolysis of the samples took place in a tubular furnace operated under inert argon atmosphere at various temperatures (900-1500°C). A typical heating cycle involved heating to 550°C at 10°C/min, held at this temperature for 60 min, then a second ramp to the final temperatures at 10°C and held the sample for 60 min and finally cooling the samples to the room temperature. To prepare ceramic composites, inert and active powders were mixed with the polymers at various ratios in the range of 60-80 wt% to obtain green bodies. Blends were casted in metal moulds, partially stabilized in an oven at 150°C and then uniaxially pressed using a hot press under 15 MPa at 220°C for 2 hours for complete curing. Green bodies were finally pyrolyzed following a multi-step heating schedule described above.

2.2. Sample Characterization Techniques

Pyrolysis products of both neat and filler added samples were identified by X-ray diffraction (XRD) technique using Philips X'Pert Pro diffractometer, with $\text{CuK}\alpha$ radiation. Infrared spectroscopy technique (FTIR) was also used to identify the phase changes during pyrolysis using Nicolet Magna-IR 550 Spectrometer. Polished samples were prepared for microstructural characterization. Philips XL 30SFEG field emission scanning electron microscope (SEM) and attached energy dispersive X-ray (EDX) spectrometer was utilized to analyze polished and fractured specimen surfaces. Vickers indentation test were performed on polished samples with HV2 (20N) using Zwick/Roell-TestX'Pert V9.0 machine. The indentation tip displacement rate was selected as 0.2 mm/min.

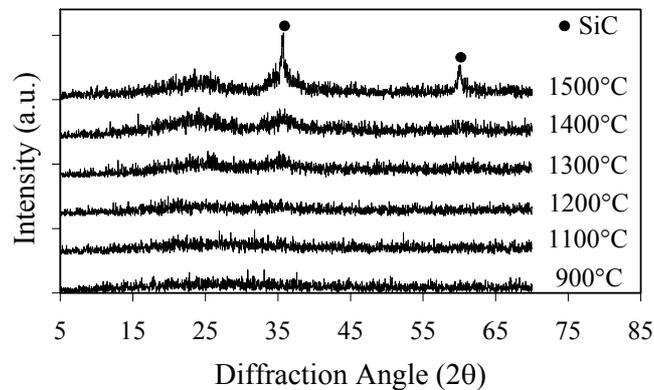
2. RESULTS & DISCUSSION

Green bodies were obtained after polymerization of the precursors at 220°C. The stability of green bodies indicated the network formation. These formations were studied by IR spectroscopy and X-Ray diffraction. Fig. 1 shows the infrared spectra of the neat PMS polymer processed at various temperatures. The spectra give the vibration bands of 770 (asym. ν Si-CH₃), 1030 (Si-OR), 1120 (Si-O-Si), 1280 (sym. Si-CH₃) and a broad band between 2000-3000 (SiOC-H) for the samples prepared at 220°C. After pyrolysis of the samples above 1100°C, C-H absorption bands can not be detected.

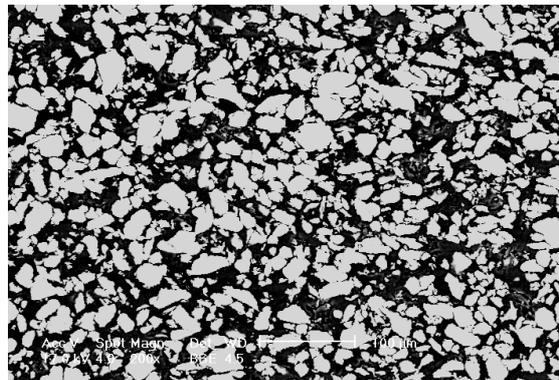


“Fig. 1. FTIR of the neat PMS polymerized at 220°C and pyrolyzed under Ar at various temperatures.”

The thermal conversion from organic siloxane network into the inorganic ceramic structure was also investigated using XRD method. Fig. 2 shows the XRD patterns of the neat PPS samples heated to different temperatures. The patterns up to 1300°C are characteristic of amorphous materials of SiO_xC_y . The broad peaks with low intensities at above 1300 °C are the diffractions associated to β -SiC. The peaks of $2\theta=36^\circ$ and 60° at 1500°C are characteristic for β -SiC crystals. The CMC monoliths with inert and active fillers were also synthesised by pyrolysis technique under Ar. Fig.3 is an example of the BSE micrograph of CMC green bodies prepared with 70 wt% Ti / PMS and cured at 220°C. In the image, white and black regions represent Ti and PMS, respectively. It is seen that a homogenous distribution of the particulates within the polymer matrix is obtained after the mixing and hot pressing stages.

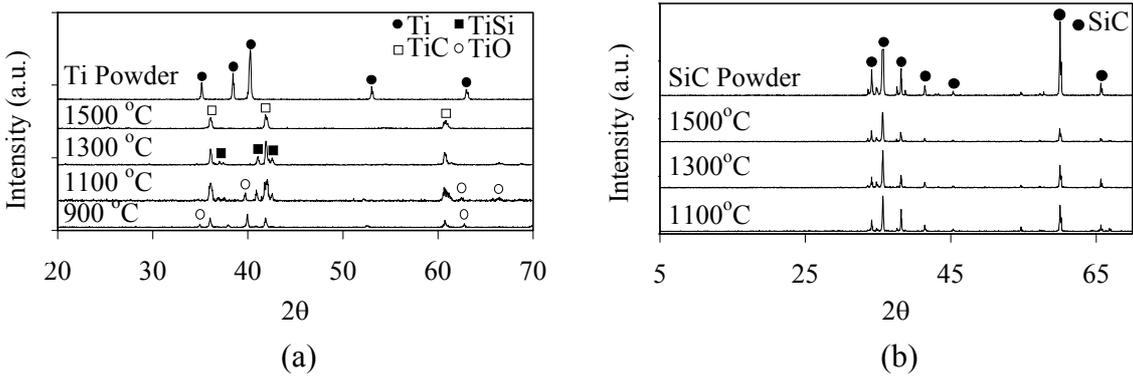


“Fig. 2. X-ray diffraction patterns of the neat PPS pyrolyzed under Ar at various temperatures.”

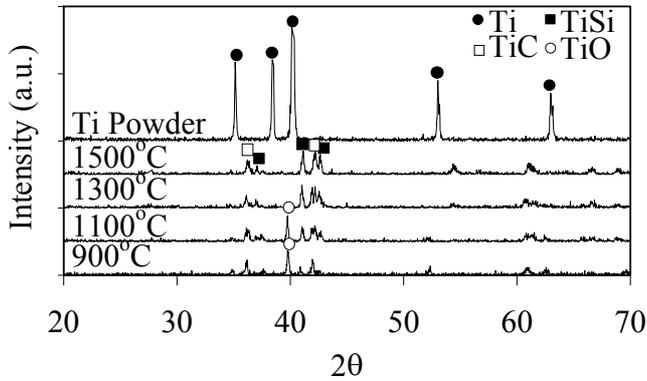


“Fig.3. Polished surface BSE micrographs of 70 wt% active Ti filled PMS.”

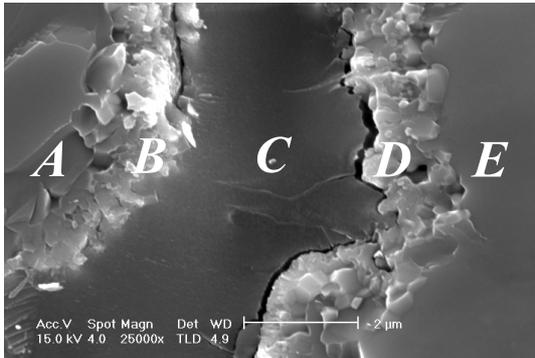
Fig. 4 shows the XRD patterns of the active (Ti) and inert (SiC) particulate added CMCs prepared from PPS at various temperatures. The results showed that with the use of active fillers formation of TiC, TiSi and TiO within the amorphous matrix occurred due to the reactions between the Ti and the polymer decomposition products. However, no new phase development was observed in the case of inert SiC particulate addition. Fig. 5 shows the XRD patterns of the Ti added CMC monoliths prepared from PMS at various temperatures. Similar to PPS, pyrolysis of Ti/PMS green bodies yields the formation of TiC, TiSi and TiO phases. The phase developments were also monitored using SEM-EDX analysis. As an example, fracture surface SEM image of 80 wt% Ti filled CMC prepared at 900°C from Ti/PMS bodies is shown in Fig.6. Also, elemental distributions along the line A to E are given in Table 1.



“Fig. 4. X-ray diffraction patterns of (a) 60 wt% Ti/PPS, (b) 60 wt% SiC/PPS pyrolyzed under Ar at various temperatures.”



“Fig. 5. X-ray diffraction patterns of 60 wt% Ti/PMS pyrolyzed under Ar at various temperatures.”



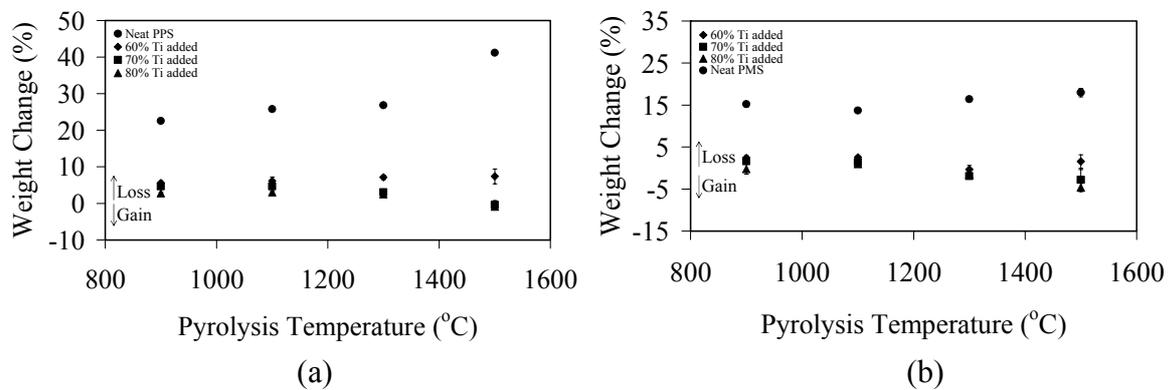
“Fig. 6. Fracture surface SEM micrograph of 80 wt% Ti filled CMC monolith prepared from Ti/PMS bodies at 900°C. Magnification 25000X.”

“**Table 1.** Elemental distributions along the line between two adjacent Ti rich particulates for 80 wt% Ti filled CMC monolith prepared from Ti/PMS bodies at 900°C.”

Region	C wt%	Si wt%	Ti wt%	O wt%
A	2.71	3.91	82.06	11.33
B	2.96	17.22	43.79	36.03
C	4.69	46.76	7.06	41.49
D	3.98	11.78	71.35	12.89
E	2.05	0.65	80.03	17.26

As seen from the table, regions A and E are Ti rich and a matrix region with some compositional gradients may form between the adjacent Ti particulates. The matrix may consist of the decomposition products of the preceramic polymers and their reaction with Ti powder. Region B and D may compose of TiO, TiSi and TiC while Region C is SiOC rich phases. On the other hand, at pyrolysis temperatures above 1100°C, these distinct phases can not be detected evidently. At elevated temperatures, compositional gradients and also the interphases may diminish due to extensive reaction/diffusion of the filler and pyrolysis products. This may give more homogeneous distribution of the elements in the ceramic structure.

Carbothermal reductions in Si-O-C systems may leads to the formation of gaseous products that causes weight losses and finally a deterioration of mechanical properties. Fig. 7 shows the weight changes of the neat and active filler added samples at various pyrolysis temperatures. For pyrolysis in the range of 900-1500°C, phenyl containing precursor, PPS lose its weight of 22-40 %, while methyl containing precursor PMS lose 15-17 wt%, respectively. The lower mass loss of PMS is due to high carbon content of this polymer.

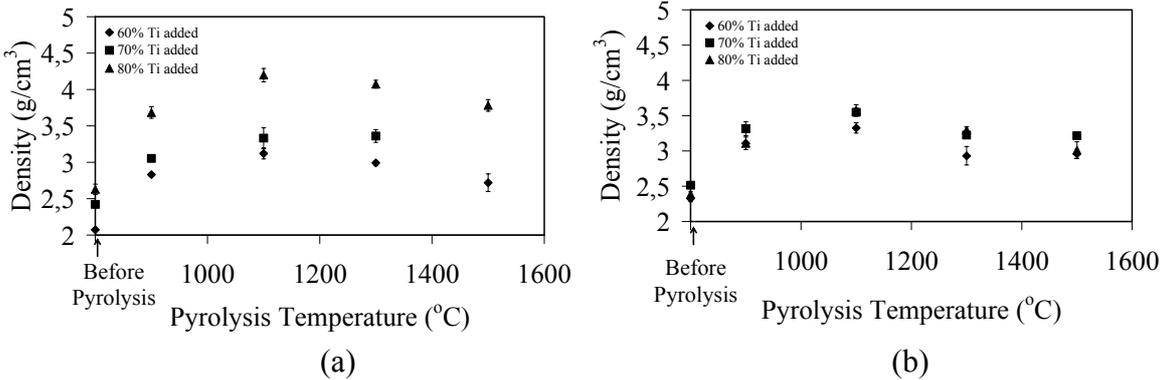


“**Fig.7.** Weight changes values as a function of pyrolysis temperature for samples of (a) 0, 60, 70, 80 wt% Ti added PPS (b) 0, 60, 70, 80 wt% Ti added PMS.”

Weight changes are considerably affected in the case of active Ti fillers are incorporated into the ceramic structure due to the reduction of the polymer ratio and the reactions between polymer and filler particles. Weight change values are also different for the composites made with PMS and PPS. Note that a weight gain (negative values) was observed for Ti/PMS samples especially at higher temperatures. Weight gain of 4.63 % was measured for 80% Ti added PMS samples while a weight loss of 0.89 % was measured for 80% Ti added PPS for pyrolysis at 1500°C.

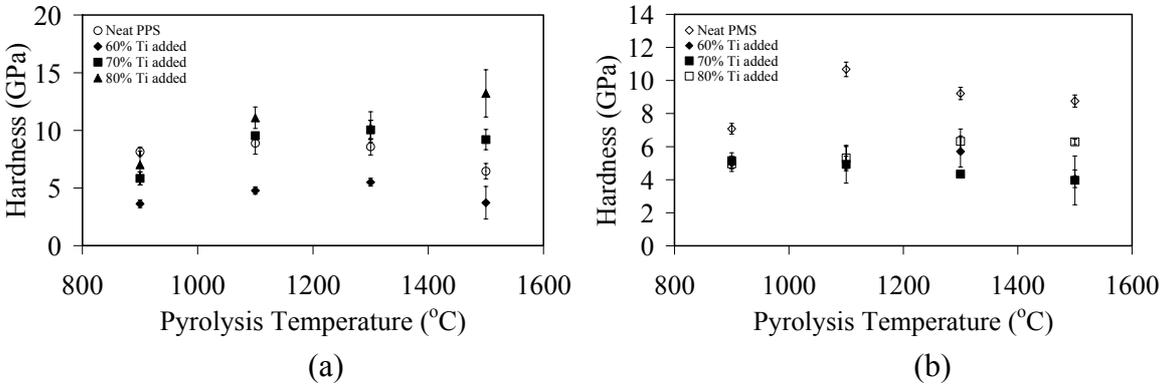
Polymer to ceramic conversions may also lead to an increase in the density and densification may result in the formation of cracks in the microstructure of the pyrolysis product. Densification during organic to inorganic conversion can be controlled by incorporation of the active fillers by reducing the polymer ratio and promoting the reactions between the polymer decomposition products and the filler particles to control the shrinkage, porosity formation and microcracking. Effects of the type of the polymer and pyrolysis temperature on the final

densities of the ceramic monoliths made with PPS and PMS is shown in Fig. 8. The density of the green bodies was measured in the range of 2-2.7 g/cm³ before pyrolysis. The highest density values for CMCs were obtained with addition of 80 wt% Ti (4.20 ± 0.1 g/cm³ is the highest) in PPS samples, however, the effect of the filler ratio in PMS samples were found to be negligible. Also, the results showed that pyrolysis temperature has some important effect on the densification behaviour. It was observed that the density values are the highest at 1100°C and it is the optimum point to manufacture crack-free samples with the lowest porosity.



“Fig. 8. Density values for the samples prepared with addition of 60, 70, 80 wt% Ti into (a) PPS, (b) PMS as a function of pyrolysis temperature.”

Hardness tests were carried out to evaluate the effects of pyrolysis temperature and filler addition into the polymers on the mechanical behaviour of the composites. The hardness values as a function of temperature are shown in Fig.9 for pyrolyzed neat polymers and their composites with Ti addition. It was found that neat ceramics reach the maximum hardness values (8.88 GPa for neat PPS, 10.67 GPa for neat PMS) at 1100°C, which is the optimum temperature for crack free samples with the least amount of porosity. However, the polymers exhibited distinct behaviour by the incorporation of Ti particulates. For PPS, at low concentrations and pyrolysis temperatures, the addition of Ti reduced the hardness values, however, at concentrations above 70 wt% resulted in the higher values (up to 13.20 ± 2.05 GPa) as compared with those with neat polymer. On the other hand, for PMS, addition of Ti reduced the hardness of composites for all concentrations.



“Fig.9. Vickers hardness values as a function of pyrolysis temperature for neat ceramics and composites made with various Ti added (a) PPS and (b) PMS precursors.”

Polished surface SEM images for CMCs made with 80 wt% Ti filled PPS and PMS polymers pyrolyzed at various temperatures are illustrated in Figures 10 and 11, respectively. As seen in the figures, as the pyrolysis temperatures increases a reduction of porosity is observed for PPS, while pore fraction increases for PMS made composites. This result implies that there is a considerable effect of pyrolysis temperature, type of precursor and Ti concentration on the microstructure, densities, and hardness values of the composites.

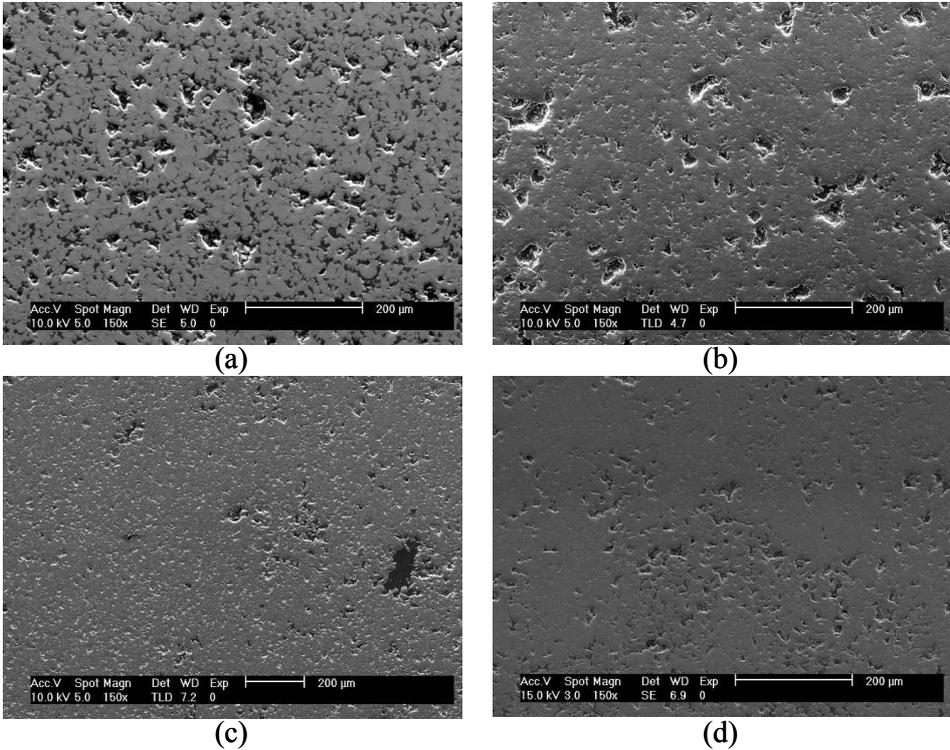


Fig.10. SEM polished surface micrographs of 80 wt% active Ti filled PPS pyrolyzed at various temperatures (a) 900, (b) 1100, (c) 1300, (d) 1500°C. Magnification 150X

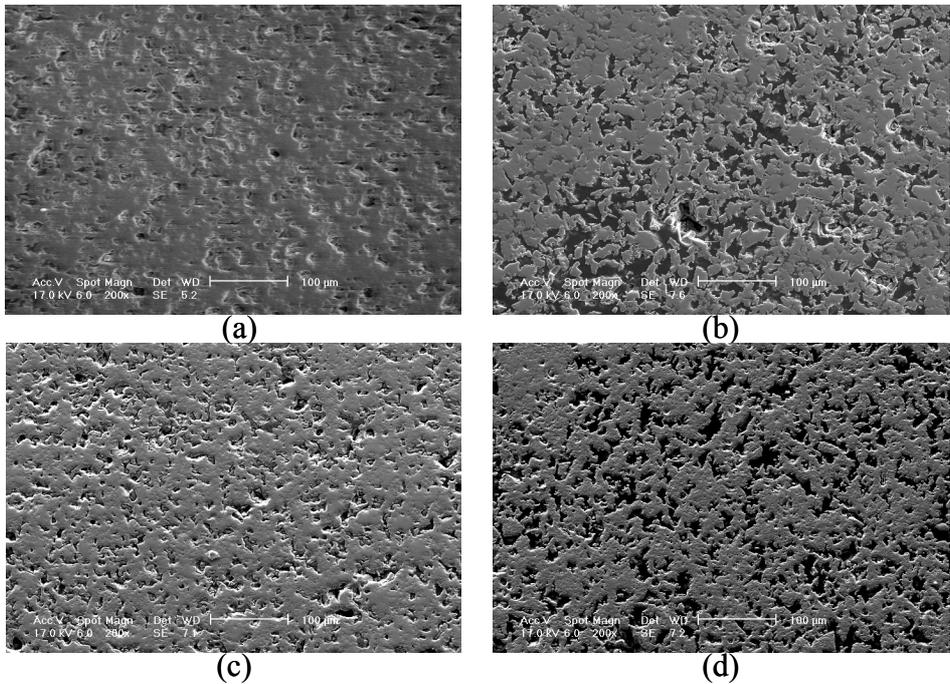


Fig.11. SEM polished surface micrographs of 80 wt% active Ti filled PMS pyrolyzed at various temperatures (a) 900, (b) 1100, (c) 1300, (d) 1500°C. Magnification 150X

3. CONCLUSIONS

Active and inert filler incorporated ceramic composites were developed based on the pyrolytic conversion of – phenyl and – methyl containing polysiloxanes. It was found that the thermal transformation of the neat polymers yields amorphous silicon oxycarbide (SiO_xC_y) ceramics at temperatures below 1300°C, however, at higher temperatures (~1500°C) crystalline β -SiC phases forms. Active fillers compensate the mass losses by reaction of active filler and decomposition products of the polysiloxanes. Formation of new phases; TiC, TiSi and TiO within the amorphous matrix occurs due to the reactions between the active Ti particulates and the polymers. It was found that the precursor and filler type, filler concentration and pyrolysis temperature has some considerable effect on the microstructure, phase development, mass losses, densification and mechanical behavior of composites. Weight changes are considerably affected in the case of active Ti fillers are incorporated into the polymer systems. Furthermore, a weight gain may be observed for Ti/PMS composites especially at higher temperatures. The highest density values for CMCs are obtained with the addition of 80 wt% Ti in PPS samples, however, the effect of the filler ratio in PMS samples were found to be negligible. The results imply that pyrolysis temperature has some significant effect on the densification behaviour. It was also found that neat ceramics reach the maximum hardness values at 1100°C, which is the optimum temperature for crack free samples with the least amount of porosity. However, the polymers exhibited distinct behaviour by the incorporation of Ti particulates. Only for PPS, at concentrations above 70 wt% higher hardness values were measured as compared with those with neat polymer.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from The Scientific and Technical Research Council of Turkey (TÜBİTAK) for MİSAG 215 project.

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