Preparation of silicon oxycarbide amorphous ceramics from polymer precursors and the characterization of their high temperature stability

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Silicon oxycarbide amorphous ceramics have carbon atoms in glass networks and have a higher level of elastic modulus, hardness, and high temperature viscosity than silicon dioxide. In this study, silicon oxycarbide ceramics were prepared by heat treatment of polymethyl and polymethylphenyl silsesquioxane polymer precursors at 1000-1500 $^{\circ}$C in an argon atmosphere. The silicon oxycarbide ceramics prepared were found to have amorphous structures and compositions of SiO_xC_y where x = 1.40-1.46, y = 0.57-0.70 or x = 1.44-1.53, y = 2.60-2.68 depending on the type of precursor. Silicon oxycarbide amorphous ceramics made from polymethylphenyl silsequioxane were unstable at high temperatures, showing a weight loss of 24% in air and 4% in argon during thermogravimetric analysis. Silicon oxycarbide amorphous ceramics made from polymethyl silsesquioxane precursor were stable in argon at 1500 $^{\circ}$C without loss of weight or crystallization. However, they showed weight losses of 1.7 and 2.8% in air at 1500 and 1650 $^{\circ}$C, respectively.

Key words: Silicon oxycarbide glass, Polymer-derived ceramics, High temperature stability, Oxidation resistance.

Introduction

Hard ceramics like carbides, nitrides, and borides have a high strength, thermal resistance, and corrosion resistance and are used for structural parts at room or high temperatures either in the form of bulk or a film. An example of film application is a thermal and oxidation resistant coating for carbon-carbon composites or graphite. The ceramic coating could seal the surface of carbonaceous materials and successfully prohibit the oxidation at high temperatures. But ceramics are brittle and can fail under an applied or thermal stress by fast crack growth. Recently, Yun, et al., studied an oxidation resistive multilayer silicon carbide coating for carbon-carbon composites and found a silicon oxycarbide amorphous layer in the middle was effective in healing cracks and lengthening the life time of composites at a temperature as high as 1500 $^{\circ}$C [1]. Also, Kang and Yun reported the healing capability of a silicon oxycarbide glass coating on silicon carbide bulk ceramics [2].

Silicon oxycarbide amorphous ceramics have similar network structures to the one that silicon oxide glasses have except that some oxygen atoms are replaced by carbon atoms. Since a carbon atom has four ligands while an oxygen atom has two, silicon oxycarbide is more advantageous to form a network structure than silicon oxide. In fact, silicon oxycarbide amorphous ceramics have better mechanical and physical properties than silicon oxide (Table 1). For example, silicon oxycarbide has a 40% higher elastic modulus, 20% higher hardness, and 160 degree higher glass transition temperature than silicon oxide [3-6].

Silicon oxycarbide amorphous ceramics can be made by the solid state reaction between silicon oxide and carbon or silicon carbide [7], but may also be prepared from polymer precursors [8]. The advantage of the polymer precursor method over the solid state reaction method is that the method and temperature are simple and low. One of the candidate polymer materials having silicon, carbon, and oxygen elements are silsesquioxanes such as polymethyl silsesquioxane, polyphenyl silsesquioxane, and polymethylphenyl silsesquioxane. In this research, silicon oxycarbide amorphous ceramics were prepared using polymethyl and polymethylphenyl silsesquioxane which have relatively simpler structures.

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Table 1. Properties of silicon oxycarbide glass and silicon oxide glass [3].

Properties	SiOC	SiO_2
Density (g/cm^3)	2.35	2.20
Thermal expansion coefficient (10^{-6}/K)	3.14	0.5
Vickers Hardness (GPa)	7.0-8.6	6.0-7.0
Elastic Modulus (GPa)	97.9	70
Glass transition temperature (degee C)	1350	1190
Refractive index	1.58	1.46
Dielectric constant	4.4	4
Electric conductivity (/Ω. cm)	4×10^{-13}	$\sim10^{-22}$

Experimental Procedures

Silicon oxycarbide amorphous ceramics were prepared using two types of polymer precursors: polymethyl silsesquioxane and polymethylphenyl silsesquioxane (GE Toshiba). These polymer powders were first dissolved in a solvent, such as ethanol, toluene, or xylene and dried. The dried powders were decomposed by heating at 1000, 1150, 1300, or 1500 °C in an argon atmosphere. Decomposed powders were examined by X-ray powder diffractometry (XRD) for phase analysis, transmission electron microscopy (TEM) for microstructural and phase analyses, and an electron probe microanalyzer (EPMA) for composition analysis. They were also examined by thermogravimetry (TG) during heating in an argon or air atmosphere.
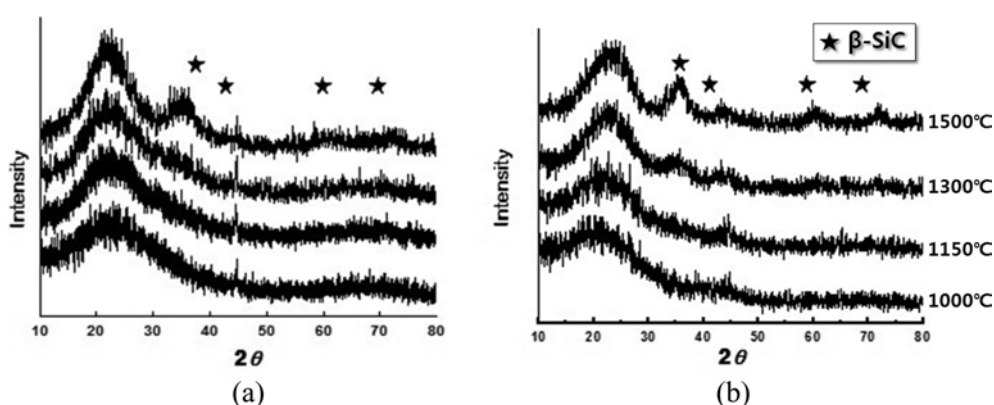
Since the silicon oxycarbide made from polymethyl silsesquioxane showed better thermal properties, further tests of high temperature stability and oxidation resistance were performed on this ceramic. Test samples were prepared by the pyrolysis of polymers at 1150 °C in an argon atmosphere. Oxidation resistance was tested by heating in an air atmosphere at 1500 or 1650 °C for 6, 12, 18, or 24 hours and by measuring weight changes. High temperature stability was tested by heating test samples at 1500 °C for 24 hours in an argon atmosphere and by measuring weight changes.

Results and Discussion

Preparation of silicon oxycarbide ceramics

Black lustered materials were formed after the decomposition of the polymer precursors in both cases. X-ray diffractometry analysis for the ceramics prepared from polymethyl silsesquioxane showed a broad peak at and near 22 degrees by the diffraction from the silicon-oxygen primary bonding in an amorphous structure (Fig. 1) [9, 10]. When the polymers are decomposed by heat treatment at 1500 °C, other broad peaks at 36, 41, 60, and 72 degrees were formed. These peaks show that the beta silicon carbide phase was formed. Since the widths of these peaks are not narrow, the crystals must be in the order of nanometre size. The ceramics from polymethylphenyl silsesquioxane also show similar results but in this case the silicon carbide diffraction peaks were formed at temperatures as low as 1300 °C implying that the crystallization temperature is lower by 200 °C than for the polymethyl silsesquioxane case. TEM investigation also showed that all samples had amorphous structures. The samples prepared at 1500 °C were found to

Fig. 1. XRD patterns for the ceramics prepared from (a) polymethyl silsesquioxane, and (b) polymethylphenyl silsesquioxane. Note that 44° peak is from the holder.
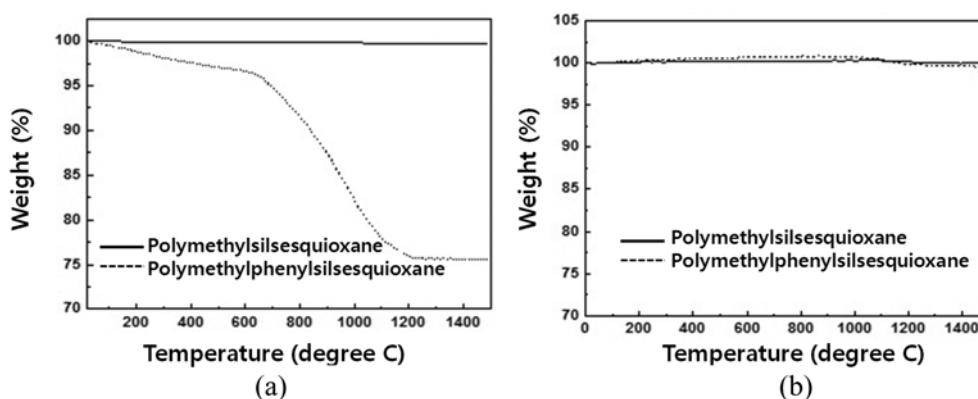
Fig. 2. Weight change of silicon oxycarbide ceramics made from two types of polymers as a function of temperature during the thermogravimetric (TG) analysis (a) in an air and (b) in an argon atmosphere.

have small numbers of graphite and silicon carbide nanocrystals grown in the amorphous matrix.

Compositions of the ceramics prepared by decomposition of polymethyl silsesquioxane at 1000, 1150, 1300, or 1500 °C were $SiO_{1.46}C_{0.57}$, $SiO_{1.40}C_{0.70}$, $SiO_{1.42}C_{0.55}$, $SiO_{1.42}C_{0.60}$, respectively as determined by EPMA. The ceramics prepared were silicon oxycarbide which had 1.4-1.5 oxygen atoms and 0.6-0.7 carbon atoms for each silicon atom. The sum of the numbers of oxygen and carbon atoms is 2.0-2.1, which is similar to two which silicon oxide has for each silicon atom. On the other hand, the compositions of the ceramics prepared by decomposition of polymethylphenyl silsesquioxane at 1000, 1150, 1300, and 1500 °C were $SiO_{1.53}C_{2.60}$, $SiO_{1.46}C_{2.63}$, $SiO_{1.46}C_{2.65}$, and $SiO_{1.44}C_{2.68}$, respectively as determined by EPMA. The ceramics prepared were silicon oxycarbide which had 1.4-1.5 oxygen atoms and 2.6-2.7 carbon atoms for each silicon atom. These ceramics have two more carbon atoms for each silicon atom compared with those from polymethyl silsesquioxane. This is because a methylphenyl group $[CH_3(C_5H_6)]$ has a higher number of carbon atoms than a methyl group $[CH_3]$. The ligands of C-O, or C-H in these polymers were decomposed to form carbon oxide, hydrogen, or hydrocarbon molecules which are easily removed. The remaining silicon, oxygen, and carbon atoms form silicon oxycarbide networks with basic structures of $[CSiO_3]$, $[C_2SiO_2]$, $[C_3SiO]$, and $[C_4Si]$ [6].

When the silicon oxycarbide ceramic samples prepared from polymer precursors were heated to 1500 °C for thermogravimetric analysis, the weights of samples prepared from polymethyl silsesquioxane polymers decreased 0.3% in air and 0% in argon, while those from polymethylphenyl silsesquioxane polymers decreased 24% in air and 4% in argon, showing that the the former is more stable at high temperatures than the latter (Fig. 2). The silicon oxycarbide ceramics made from polymethyl silsesquioxane has a lower number of carbon atoms and may have more stable networks than the other silicon oxycarbide ceramics [8, 11].
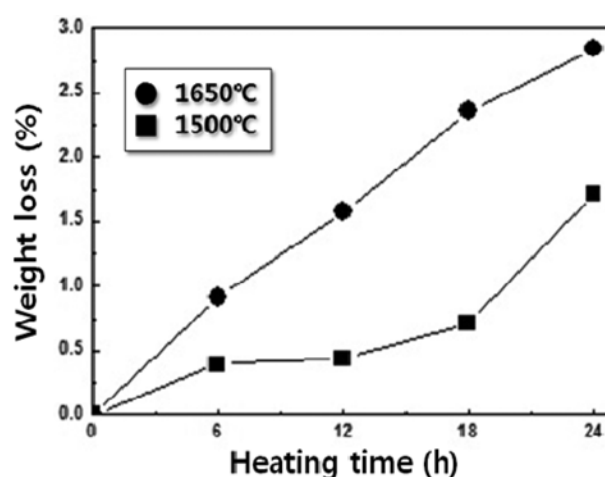

Fig. 3. Weight loss of silicon oxycarbide amorphous ceramics during high temperature oxidation tests at 1500 and 1650 °C.

High temperature oxidation resistance test

Since the silicon oxycarbide ceramic made from polymethyl silsesquioxane polymer is more stable, it was considered to be a candidate for a future high temperature application. High temperature stability and oxidation resistance tests were performed for the selected ceramic. The samples became light bluish or white without luster after the oxidation resistance test for 24 hours at 1500 or 1650 °C, respectively, showing surface degradation. As shown in Fig. 3, the weight loss during the oxidation resistance tests was up to 1.7% and 2.8% at 1500 and 1650 °C, respectively. The amount of weight loss was not serious but since it increased in a linear way with time, especially at 1650 °C, this silicon oxycarbide amorphous ceramic would not resist oxidation effectively when it is exposed to an oxidation atmosphere at 1500 °C or a higher temperature for a longer time.

Phase change was examined with X-ray diffractometry after the high temperature oxidation resistance test. As shown in Fig. 4, cristobalite, one of the high temperature crystalline phases of silicon oxide, was formed, showing degradation of the glass at high temperature. At 1650 °C,
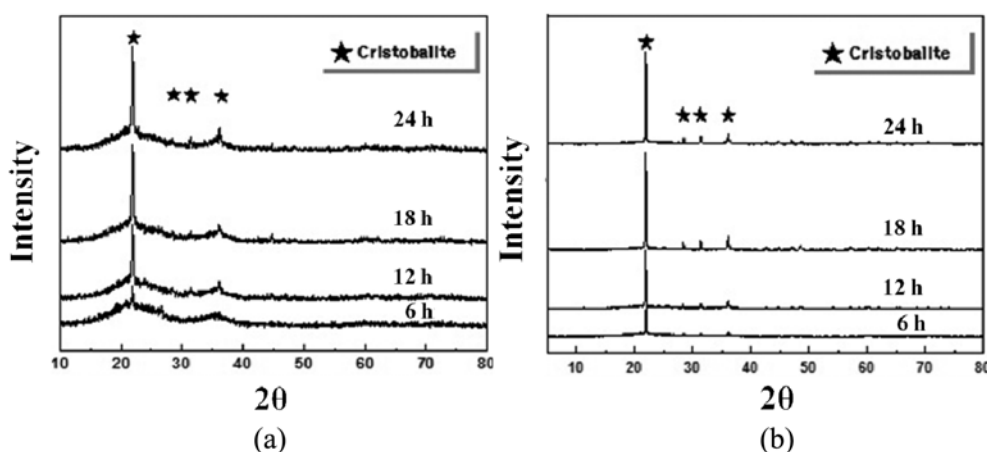

Fig. 4. X-ray diffraction patterns for the silicon oxycarbide ceramics after the oxidation resistance tests at (a) 1500, and (b) 1650 °C.
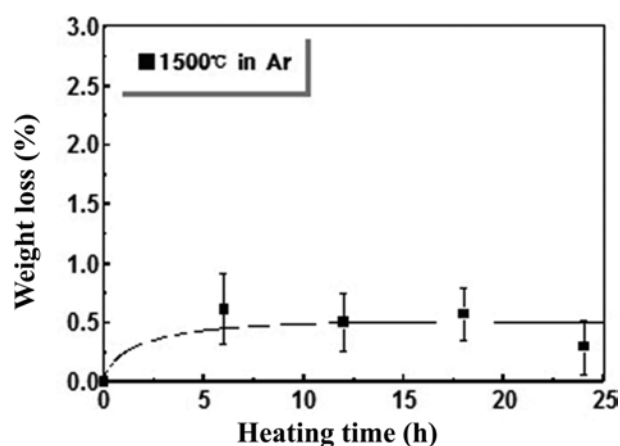
Fig. 5. Weight loss of silicon oxycarbide amorphous ceramics during a high temperature stability test at 1500 °C in an argon atmosphere.
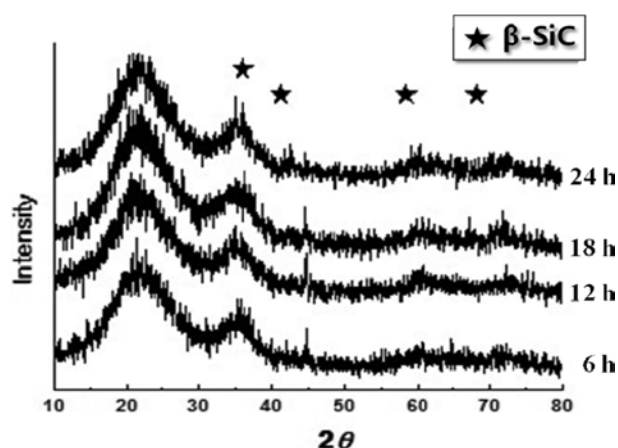

Fig. 6. XRD pattern of silicon oxycarbide ceramics after high temperature stability tests at 1500 °C for various periods of time.

the degradation was more serious. The composition of silicon oxycarbide ceramic changed from $SiO_{1.40}C_{0.70}$ to $SiO_{1.48}C_{0.60}$ or $SiO_{1.50}C_{0.62}$ after the test at 1500 or 1650 °C, respectively, showing that the oxygen content increased while the carbon content decreased. This may show that network carbon atoms on the sample surface react with oxygen in the air, forming carbon monoxide gas which is removed easily, and the vacant sites are filled with oxygen from the air.

High temperature stability test

A high temperature stability test was performed for the silicon oxycarbide amorphous ceramic in argon at 1500 °C for 24 hours. As shown in Fig. 5, the weight loss was less than 0.5% after the test. But the samples looked lusterless after the test showing the surface was degraded. XRD result showed that a considerable amount of beta silicon carbide nanosize crystals were formed after the test (Fig. 6). The composition changed from $SiO_{1.40}C_{0.70}$ to $SiO_{1.54}C_{0.63}$ or $SiO_{1.53}C_{0.64}$, after 6 or 24 hours of test, respectively.

The results show that the silicon oxycarbide amorphous

ceramics were unstable in air but stable in an argon atmosphere even at high temperatures. If they are used in a non-oxidizing atmosphere, they may serve well without degradation. If they are coated with an oxidation resistive film, they can be used even in an oxidation atmosphere at high temperatures. In particular, if the silicon oxycarbide amorphous ceramic coating film is prepared with a combination of an outer layer of a protective coating film, it may withstand oxidation as well as degradation at high temperatures for a considerable life time.

Conclusions

Silicon oxycarbide ceramics were successfully prepared from polymethyl and polymethylphenyl silsesquioxane polymer precursors. Both ceramics had amorphous structures and compositions of SiO_xC_y, where x = 1.4-1.5, y = 0.6-0.7 for the former, and x = 1.4-1.5, y = 2.6-2.7 for the latter, depending on the type of polymer precursor. Silicon oxycarbide amorphous ceramics were very stable in argon at high temperatures without weight loss. They were less stable in air and lost weight of 1.7% or 2.8% at 1500 or 1650 °C, respectively. The silicon oxycarbide ceramics prepared from polymethyl silsesquioxane was relatively more stable both in air and in argon than those from polymethylphenyl silsesquioxane. The results show that silicon oxycarbide amorphous ceramics can be used in a high temperature application if it is not exposed to air or if the exposure time is limited.

Acknowledgement

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