Silicon Carbide Coated Graphite Derived from Chlorine Free Preceramic Polymer Precursor

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Abstract
Graphite is widely used in electronic industry due to its excellent electrical and thermal properties. However, graphite starts to oxidize around 350°C which seriously degrades its properties. SiC coating can be applied to graphite to improve its high temperature oxidation resistance. In this research, SiC coating on graphite was made via preceramic polymer using a polymethylphenylsilane. 20% of polymethylphenylsilane in hexane solution was coated onto graphite by dip coating method. After coating, thermal oxidation was carried out at 200°C for crosslink of the preceramic polymer and the sample were pyrolysized at 1200°C under nitrogen to convert the preceramic polymer to SiC film. The phase formation, stoichiometry and microstructure of the SiC coating after pyrolysis were investigated using low angle XRD and FESEM etc. Oxidation resistance up to 600°C was evaluated.

Introduction
Graphite is widely used as heater, semiconductor hardware parts or brazing zig etc. in electronic industry due to its low thermal expansion, high thermal conductivity, chemical inertness and its high melting point. However, graphite starts to oxidize around 350°C, where the physical properties of the graphite are degraded due to severe oxidation at high temperature. In such aspect, SiC is a promising material to be used as protective coating layer on graphite materials due to its outstanding thermal stability and hardness⁴. Generally, SiC coating has been carried out via chemical vapor deposition using methyltrichlorosilane as an organometallic precursor. However, the use of methyltrichlorosilane as an organometallic precursor generates HCl gas, which is highly corrosive and toxic. Therefore, it is required to find alternate route to be coated SiC using an environmentally-benign process.

In this research, SiC coating was carried out onto graphite substrate from Cl free preceramic polymers such as polyphenylcarbosilane using dip coating method. After coating, the crosslinking of the polyphenylcarbosilane was carried out at 200°C in the air for 10 min, and then the sample was heated under Ar at 1200°C for 1 h to convert to SiC film.

Experimental
Preparation of Polydimethylsilane
Polymethylphenylsilane was synthesized through the reaction of methylphenyl dichlorosilane with sodium metal in toluene solvent at 110°C. (Fig.1) Metallic sodium was chopped into small pieces and transferred into toluene under inert atmosphere. At 110°C, after sodium was entirely dispersed into toluene solvent, methylphenyl dichlorosilane was dropwised and refluxed for 7 h. After the reaction, the remains of sodium metal were removed by adding methanol. To remove NaCl and low molecular weight of polymethylphenylsilane, the solid product was washed thoroughly with deionized water and acetone. The final product of white precipitate was dried under vacuum.
Preparation of Polyphenylcarbosilane

For the preparation of polyphenylcarbosilane, polydimethylsilane was loaded into reaction vessel. After purging the sample with nitrogen gas, the temperature was increased to 350°C and kept for 6 hours and temperature was raised to 400°C and kept for another 6 hours. After the reaction, yellow viscous solid was obtained.

The product was dissolved in cyclohexane and filtered to remove insoluble product, and then cyclohexane was evaporated using rotary evaporator. Yellowish brown viscous product was obtained with 60% of yield. It was heated under nitrogen atmosphere at 250°C for 30 min to remove low molecular weight of polyphenylcarbosilane. The value of $M_w$ (weight average of molecular weight) of final product measured using a Gel Permeation Chromatography was 2,140.

Nanoporous SiC coating on alumina plate

The 20wt.% polyphenylcarbosilane in cyclohexane was dip coated onto graphite substrate. Then, the surface layer was converted into amorphous SiC layer by heat treatment at 600°C with heating rate of 2°C/min and followed by heat treatment at 1200°C for 1 h with heating rate of 10°C/min under inert atmosphere.

Results and discussion

The formation of the polyphenylcarbosilane is confirmed by FT-IR spectrum. Particularly, the band at around 1035 cm$^{-1}$ is very strong and assigned to CH$_2$ bending vibration in Si-CH$_2$-Si group, indicating the formation of the polyphenylcarbosilane by Kumadar rearrangement of polymethylphenylcarbosilane. These results are in agreement with those reported in the literature. The TGA curve exhibits large amount of weight loss up to 700°C due to conversion of polyphenylcarbosilane to SiC ceramic.(Fig. 2) This means that the organic groups of the polyphenylcarbosilane are decomposed below this temperature range. The ceramic yield calculated from TGA is about 70wt.%. In order to examine the pyrolysis residue, the sample after heat treatment at 1,200°C for 1 h under Ar atmosphere was crushed into a powdered form and analyzed with XRD. The diffraction peaks of the sample around 35°, 60°, and 73° corresponded to the 2 theta of the β-SiC. (Fig. 3)

The SEM microstructure of SiC coated graphite after heat-treated at 1200°C under nitrogen gas atmosphere was shown in Fig. 4. The SiC film prepared from dip coating at 3,000 rpm using 20wt.%
of polyphenylcarbosilane solution in cyclohexane doesn’t show any crack on the surface after heat treatment. The average thickness of the SiC membrane is about 2 µm. (Fig. 4) As we seen in Fig. 5, thermo resistance of SiC coated graphite has been improved tremendously compared with that of uncoated graphite. After exposure at 600°C for 800 minutes, rate of residue in case of the uncoated graphite is only 50%. The weight loss is attributed the oxidation to carbon dioxide of graphite above 350°C. However, the weight of SiC coated graphite remains more than 90% after exposure at 600°C for 800 minutes.

Conclusion

In this work, A SiC preceramic polymer, that is polyphenylcarbosilane (PPCS), was synthesized by Kumada rearrangement of polymethylphenylsilane (PMPS) at 350°C under nitrogen atmosphere. Thermal treatment of PPCS above 900°C in a nitrogen atmosphere leads to β-SiC. To improve high temperature properties of graphite, SiC coating was applied on the surface of graphite by dip coating method using a PPCS. SiC coated graphites show tremendously improved thermo resistances than uncoated graphite at 600°C in the atmosphere.

References