Article ID: 1003－6326(2004)04－0641－04

Synthesis and characterization of polyaluminocarbosilane as SiC ceramic precursor①

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Abstract: Polyaluminocarbosilane(PACS) was synthesized by the reaction of aluminum acetylacetonate ($Al(AcAc)_3$) with polysilacarbosilane (PSCS), which was prepared by thermolysis and condensation of polydimethylsilane (PDMS). The sublimation of $Al(AcAc)_3$ could be avoided by the use of PSCS as reactant. The empirical formula of PACS was $SiC_{2.01}H_{7.66}O_{0.13}Al_{0.02}$, which has the relative molecular mass of 2 265. When the reaction of PSCS with $Al(AcAc)_3$ proceeds, an enormous decrease in the number of Si—H bonds in PSCS is observed, at the same time, gas acetylacetonate is a by-product of the reaction based on the ligands of $Al(AcAc)_3$. The reaction mechanism is found to be related to the increase in the molecular mass of PACS by the cross-linking reaction of Si—H bonds in PSCS with $Al(AcAc)_3$, which leads to the formation of Si—Al bonds.

Key words: precursor; polyaluminocarbosilane; synthesis; characterization
CLC number: TQ 343.6 **Document code:** A

1 INTRODUCTION

The synthesis method of silicon carbide fibers by preceramic polymers was developed by Yajima et al in the decade of 1970s[1-3]. Intensive investigations to development of precursors to silicon carbide fibers have been actively performed[4-6]. Of these, silicon containing polymers have been most vigorously developed. Polycarbosilane (PCS), a precursor of commercial Nicalon SiC fiber, was synthesized by thermal decomposition of polydimethylsilane (PDMS) in an autoclave at 470 ℃[1-6]. Polytitanocarbosilane, which is produced by condensation reaction of the PCS with titanium(IV) tetra-alkoxide, is a precursor of commercial Tyranno Lox M SiC fiber[7,8]. Polyzirconocarbosilane, which is synthesized by condensation reaction of PCS with zirconium(IV) acetylacetonate, is a precursor of commercial Tyranno ZM SiC fiber[9-11].

In recent years, Si-C-Al and Si-C-O-Al fibers were prepared by Ishikawa et al[12,13]. These fibers show excellent heat-resistance (up to 2 000 ℃), high strength (over 2.5 GPa) and modulus (over 300 GPa), superior creep resistance, and prominent alkali resistance. Up to date, these fibers have the best performance on high temperature resistance of SiC-based fiber. Therefore, study on the precursor of these fibers has been attracting keen interest. PACS is a precursor of Si-C-Al and Si-C-O-Al ceramic fibers. Ishikawa et al synthesized PACS by the reaction of PCS with aluminum acetylacetonate ($Al(AcAc)_3$). However, by this method when the reaction proceeded, $Al(AcAc)_3$ was easy to sublime. Furthermore, in this work, in order to reduce the sublimation of $Al(AcAc)_3$, PACS was prepared by the reaction of polysilacarbosilane (PSCS) instead of PCS with $Al(AcAc)_3$. PACS was characterized. The detailed synthesis mechanism of PACS by the PSCS with Al ($AcAc)_3$ was also clarified.

2 EXPERIMENTAL

All samples described in this experiment were manipulated in a nitrogen or argon atmosphere or in a vacuum system.

2.1 Preparation of PSCS

PDMS purchased from Xin Huo Company, which is a highly crystalline, white, incoherent powder and is insoluble in common solvents such as toluene, xylene, hexane, benzene and decomposes before melting. A 500 mL, three-neck round-bottom flask, oven-dried and flushed with nitrogen, was fitted with a thermometer, a reflux condenser, a heating mantle, a pyrolysis column, a nitrogen inlet and outlet, and a receiver setting. PDMS was added to the flask under nitrogen. Then, the heating mantle was heated to 420 ℃, the thermal treatment was stopped. The thermolysis products were collected in the receiver setting at room temperature. These products were PSCS, which are liquid and soluble in com-

① **Foundation item:** Project(59972042) supported by the National Natural Science Foundation of China
Received date: 2003－11－17; **Accepted date:** 2004－03－16
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mon organic solvents.

2.2 Synthesis of PACS

PACS was prepared by the reaction of 100 g PSCS with 4 g $Al(AcAc)_3$ (Aldrich, 99%) above 300 ℃ in a stream of nitrogen gas at atmospheric pressure. $Al(AcAc)_3$ was introduced into the bottom of the flask. PSCS covered the $Al(AcAc)_3$ in order to reduce sublimation of $Al(AcAc)_3$. After reaction, a polymerized product was obtained. It was dissolved in an xylene and solution filtered. After the solvent was removed and vacuum distilled to remove insoluble species and oligomer, a gold-colored solid polymer was obtained, which is referred as PACS.

2.3 Measurements

2.3.1 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were recorded between 4 000 and 400 cm^{-1} on a Nicolet-360 spectrometer. Solid samples were analysed as KBr pellets. For characterization of the reaction of PACS, the following treatment was applied to the FT-IR. The reaction process of PACS is represented by the change in absorbance, A, of a characteristic absorption in FT-IR spectrum. The absorbance is given by the formula $A = \log(I_0/I)$, where I_0 and I are the intensities of the incident and the transmitted light. If Lambert-Berr's law holds, $A = Kcl$, where K is the extinction coefficient, c the concentration and l the thickness of absorber. In the KBr pellet method, it is difficult to determine c and l exactly. Therefore, the reaction process of PACS was shown in the reaction time dependence of the ratio $A_\upsilon/A_{\upsilon'}$, A_υ and $A_{\upsilon'}$ are absorbances of the characteristic absorption at wave number υ and υ', respectively. The absorption at 1 250 cm^{-1} ($Si—CH_3$ deformation) was selected as the characteristic absorption at υ' without overlapping with other absorptions, and the wave numbers 2 100 cm^{-1} (Si—H stretching), 1 350 cm^{-1} (CH_2 deformation of $Si—CH_2—Si$) were selected as υ.

2.3.2 Gel permeation chromatography (GPC)

GPC measurements were taken with Waters-244. Tetrahydrofuran was used as a solvent at a flow rate of 1 mL/min at room temperature. Polystyrene standards were used for calibration.

2.3.3 Elemental analysis

Chemical analysis of PACS was made for four elements: Si (by a gravimetric method); Al (by a calorimetric method); C (by a combustion volumetric method); O (by gas analysis).

3 RESULTS AND DISCUSSION

From elemental analysis as shown in Table 1, the chemical composition of the PACS precursor was Si, 44.95%; C, 38.60%; Al, 0.78%; O, 3.40%; H, 12.27% (by difference), giving the empirical formula $SiC_{2.0}H_{7.6}O_{0.13}Al_{0.018}$. Because of the sensitivity of the PACS precursor to oxygen and moisture, absorption of oxygen or moisture could lead to the higher expected oxygen content. Oxygen can be introduced into the precursor polymer structure during its synthesis. Variations in the synthesis conditions such as the polymerization temperature will also affect the composition with a general decrease in the amount of carbon and hydrogen as the degree of polymerization of the PACS increase. The results show that the atomic ratio of the carbon to silicon in the PACS precursor is about 2∶1.

Fig. 1 shows the GPC curves of PACS and PSCS. The broad peak in the high molecular mass region of PACS's GPC curve is found to be higher than that of PSCS. The average relative molecular mass, $\overline{M}_n$ of PACS is 2 265. When the reaction of PSCS with $Al(AcAc)_3$ proceeds, the $\overline{M}_n$ increases with reaction time, but the extent of the increase in $\overline{M}_n$ becomes smaller gradually.

The FT-IR spectra of PSCS, PACS and $Al(AcAc)_3$ are shown in Fig. 2. The wave numbers corresponding to various absorption bands in the FT-IR spectra are given in Table 2. These assignments were based on data from known organic compounds and PCS[5,6]. In case of PSCS and PACS, FT-IR indicates that the major bonds presented were $Si—CH_3$ (1 250 cm^{-1}) and Si—H (2 100 cm^{-1}). On the other hand, in the case of $Al(AcAc)_3$, the characteristic absorption at 1 580 cm^{-1} (C═O stretching) and 1 515 cm^{-1} (C═C

Table 1 Chemical analysis of PACS and $Al(AcAc)_3$

Compound	w/%					Chemical formula	n(O)/n(Al)
	Si	C	O	H	Al		
PACS	44.95	38.60	3.40	12.27	0.78	$SiC_{2.0}H_{7.6}O_{0.13}Al_{0.018}$	7.2
$Al(AcAc)_3$	0	55.50	29.70	6.50	8.30	$CH_{1.4}O_{0.4}Al_{0.07}$	6.0

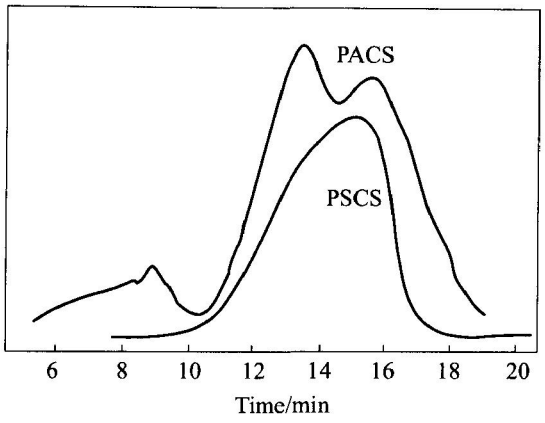

Fig. 1 GPC profiles of PSCS and PACS

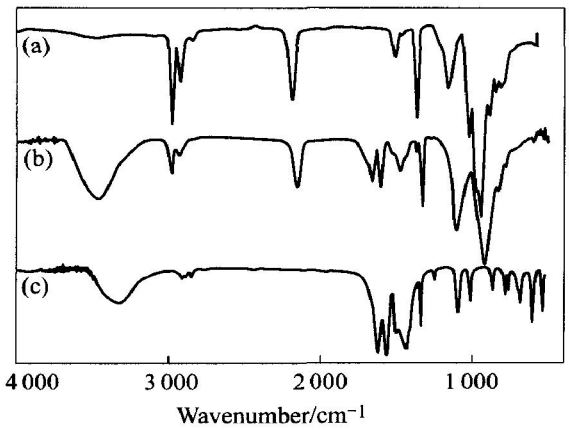

Fig. 2 FT-R spectra of (a) PSCS, (b) PACS and (c) $Al(AcAc)_3$

Table 2 Wavenumbers and assignments of FT-IR spectrum of PSCS and PACS

Wavenumber/ cm^{-1}	Mode of vibration
1850 - 700	Si—CH_3 bending
	Si—C stretching in SiC_4
950 - 800	Si—H bending
1 020	CH_2 bending in Si—CH_2—Si
1 100 - 1 000	Si—O stretching in Si—O—Si or Si—O—C
1 200	C—O stretching
1 250	Si—CH_3 stretching
1 450 - 1 350	H stretching in CH, CH_2, CH_3
1 720	C═O stretching
2 100	Si—H stretching
2 950 - 2 900	C—H stretching
3 700 - 3 200	O—H stretching in Si—OH

stretching) are observed. In the absorption of PACS, which was synthesized by the reaction of PSCS and $Al(AcAc)_3$, a tremendous decrease in the number of Si—H bond is found. Further more, in the absorption of PACS, appearance of characteristic absorptions of $Al(AcAc)_3$ is recognized. It is assumed that the reaction of PSCS with $Al(AcAc)_3$ results in the delocalization of the electron of C═O bond in $Al(AcAc)_3$ and/or the localization of the electron of C═C bond in $Al(AcAc)_3$.

Fig. 3 shows the changes of the values of $A_{2\,100}/A_{1\,250}$, $A_{1\,350}/A_{1\,250}$, corresponding to Si—H, Si—CH_2—Si bond respectively, in PACS during the reaction of PSCS with $Al(AcAc)_3$. As described above, an enormous decrease in the number of Si—H bond is observed at the beginning of the reaction, whereas no change in the number of Si—CH_2—Si bond is recognized.

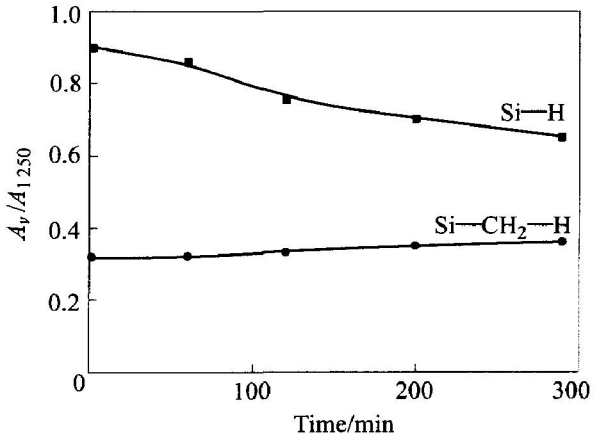

Fig. 3 Changes in Si—H and Si—CH_2—Si bonds of products during reaction of PSCS with $Al(AcAc)_3$

On the other hand, Cao et al[14, 15] researched the reaction of PSCS with $Al(AcAc)_3$ by virtue of Gas Chromatograph Mass Spectroscopy (GC-MS). The result of GC-MS analysis showed that the acetylacetonate was a by-product of the reaction based on the ligands of $Al(AcAc)_3$. The chemical analysis of the obtained PACS is shown in Table 1. As can be seen from these results concerning contents of O, it is considered that about one third of ligands of $Al(AcAc)_3$ remains in the PACS after the reaction.

From the aforesaid increase in the molecular mass with decrease in the number of Si—H bond and evolution of the acetylacetonate, the following reaction scheme was considered (Fig. 4). As can be seen from this reaction scheme, the increase in the molecular mass by the cross-linking reaction with the formation of Si—Al bond was estimated.

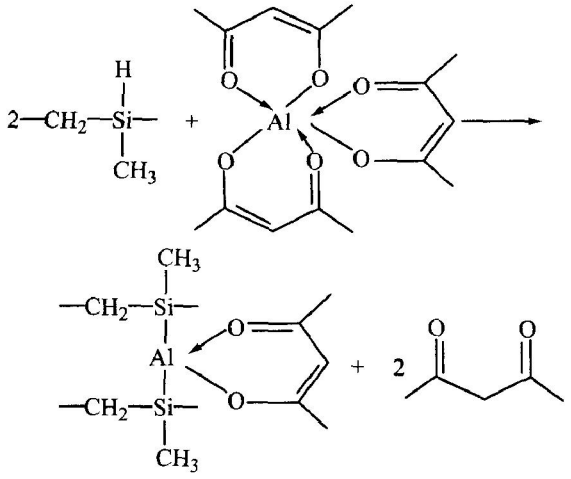

Fig. 4 Reaction scheme of PSCS with $Al(AcAc)_3$

4 CONCLUSIONS

The precursor of SiC(Al) ceramic fiber was synthesized by the reaction of $Al(AcAc)_3$ with PSCS, which was produced by the thermal decomposition and condensation of PDMS. The chemical formula of PACS was $Si_1C_{2.01}H_{7.66}O_{0.13}Al_{0.02}$. The average relative molecular mass, $\overline{M}_n$ of PACS was 2 265. The reaction of PSCS with $Al(AcAc)_3$ proceeded by the condensation reaction of Si—H bond in PSCS and the ligands of $Al(AcAc)_3$ accompanied by the evolution of acetylacetone to produce PACS. In this condensation reaction, the increase in the molecular mass by the cross-linking reaction with a formation of Si-Al bond was estimated.

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(Edited by PENG Chao-qun)