Synthesis and Ceramization of Polymethylsilane Precursors Modified with Metal Chlorides

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金属塩化物で修飾したポリメチルシラン前駆体の合成とセラミゼーション

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Polymethylsilane (PMS) modified with titanium chloride (TiCl_4) or molybdenum chloride (MoCl_5) was pyrolyzed at various temperatures to enable a detailed investigation of stable phases formed during pyrolysis. The existence of TiSi_2 in PMS- TiCl_4 precursor and $\beta\text{-MoSi}_2$ in the PMS- MoCl_5 precursor below 1273 K suggested a strong interaction between Si-H and the metal chlorides during mixing. During pyrolysis of the PMS-10 mass% TiCl_4 precursor, a silicon rich Si-Ti-C state was obtained below 973 K, which simultaneously formed crystalline Si, TiSi_2 , and SiC phases at relatively low temperatures below 1273 K. During pyrolysis of the PMS- MoCl_5 precursors, however, formation of crystalline Si and SiC phases were not accelerated, while the crystalline $\beta\text{-MoSi}_2$ or $\alpha\text{-MoSi}_2$ phase was formed rapidly. [Received June 19, 2005; Accepted March 16, 2006]

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1. Introduction

The polymer precursor method provides useful routes for synthesizing non-oxide ceramic materials with unique forms that are normally difficult to obtain using the conventional powder processing method. The microstructure of the obtained non-oxide ceramics is also unique, and varies from the amorphous to the nano-crystalline state.

Synthesis of continuous silicon carbide fiber from polycarbosilane is the most typical case that has been investigated in detail.^{1),2)} After the invention of SiC fibers, recent developments in organometallic chemistry led to the synthesis of novel precursors.³⁾⁻⁵⁾ There is now a large number of reports on various methods of precursor synthesis and utilization.⁶⁾⁻¹⁰⁾

Synthesis of a relatively new homo-polymer or co-polymer, however, is costly and takes time. For a wide range of applications, synthesis of the promising precursors using a combination of limited chemical compounds would be convenient and economical. Polymer blends of different precursors, the addition of alkoxides, or cross-linking agents, and the selection of metal fillers will be the key technologies to be addressed for the synthesis of new hybrid precursors.¹¹⁾⁻¹⁷⁾

Polymethylsilane has been employed as a precursor for silicon carbide because of its starting stoichiometric composition ($-(\text{SiH}(\text{CH}_3))_n-$). It was, however, observed that the resulting pyrolysis products always contained excess silicon due to the cleavage of Si-CH₃ bonds and CH₄ evolution.^{13),14),18),19)}

The formation of new composites with various phases have been reported by Seyferth et. al., made possible by the pyrolysis of PMS including metal fillers.^{13),20)} The process they

employed was based on a solid state reaction between inorganic Si-C amorphous and metal particles through direct ceramic-metal contacts, which could be chemically activated. Kim et al. have investigated the combination of polymethylsilane and MoCl_5 in place of Mo fillers and have reported $\beta\text{-MoSi}_2$ formation at 1273 K, which suggests a special chemical interaction between PMS and MoCl_5 .²¹⁾

In this article, a method for PMS modification using metal chlorides (TiCl_4 or MoCl_5) has been described followed by the ceramization process. Formation of titanium silicide or molybdenum silicide phase was focused during the pyrolysis process. These silicide phases intrinsically possess high temperature resistance in an oxidative atmosphere because of the formation of silica based oxide layers identical to SiC surface.²²⁾⁻²⁷⁾ In particular, SiC- MoSi_2 ceramics have been actively investigated in connection with heating element applications.

The sectile property of the resulting materials is also promising, because the complex interface between SiC- TiSi_2 or SiC- MoSi_2 , formed by the precursor method, may prevent sudden crack propagation during machining and manufacturing. The expected strong interaction between Si-H and metal chlorides during the mixing and the successive heat treatment probably yields a more complex interface than the PMS-metal filler systems examined in the previous works. The potential use of such systems in developing “nano materials” by adjusting the whole cross-linking reaction is attracting attention.

2. Experimental

2.1 Preparation of starting materials

The synthesis process for the starting polymethylsilane (PMS) by a condensation reaction of methylchlorosilane (Shin-Etsu Chemical Co., Ltd.) has been described elsewhere.^{14),28)} The PMS obtained was a pale yellow viscous liquid ($M_w=1780$, $M_w/M_n=2.0$), which has been reported to possess a partially cross-linked structure, $[(CH_3SiH)_{0.60}-(CH_3Si)_{0.40}]_n$. $TiCl_4$ and $MoCl_5$ were procured from Wako Pure Chemical Industries Ltd. and were used without further purification.

2.2 Synthesis and pyrolysis of the polymethylsilane-titanium chloride ($TiCl_4$) precursors

Mixing of $TiCl_4$ with PMS was performed in a glove box under an N_2 flow to avoid moisture contamination. A 10% PMS solution (by mass) in toluene was prepared for mixing with the $TiCl_4$. The mixing mass ratios of the PMS- $TiCl_4$ were 100-0, 90-10, 70-30, 60-40, 50-50, 40-60, and 25-75, which correspond to the Ti/Si molar ratios of 0, 0.03, 0.10, 0.16, 0.35, and 0.70. The prepared PMS- $TiCl_4$ solution was placed at the bottom of a glass tube (500 mm in length, 30 mm in diameter) equipped with a vacuum pump. After removing solvent by evaporation, the PMS- $TiCl_4$ mixture was heated at 723 K for 1 h under an Ar flow (heating rate up to 723 K was 5 K/min) to eliminate HCl from the precursor. The total mass of the PMS and $TiCl_4$ settled in the glass tube was kept at ca. 3 g. 1 g of the sample heat-treated at 723 K was placed in a quartz crucible, and was subsequently heat-treated at 1273 K by using a vertical furnace equipped with an automatic balance for in-situ thermogravimetric analysis. A 1 g sample heat-treated at 1273 K in a graphite crucible was further heated at 1573 K for 1 h in a vertical furnace equipped with $MoSi_2$ heaters.

The XRD patterns of the pyrolyzed samples were investigated (Model RINT 1100, Rigaku) using $Cu K\alpha$ radiation. Some of the pyrolysis products were mounted in epoxy resin in order to observe their polished cross-sections using an electron microprobe analyzer (EPMA JXA-870, JEOL).

2.3 Synthesis and pyrolysis of polymethylsilane-molybdenum chloride ($MoCl_5$) precursors

Mixing of $MoCl_5$ with PMS, followed by heat treatment up to 1273 K, was performed in a similar manner to that of the PMS- $TiCl_4$ mixture. The mixing mass ratios of PMS- $MoCl_5$ were 80-20, 70-30, 60-40, 40-60, and 30-70, which correspond to the Mo/Si molar ratios of 0, 0.04, 0.07, 0.11, 0.24, and 0.38. 1 g of a sample in a graphite crucible was further heated to 1773 K for 1 h in a furnace equipped with $MoSi_2$ heaters.

The XRD pattern measurements and elemental mappings on the pyrolysis products were also performed in a similar manner to those for the PMS- $TiCl_4$ systems.

3. Results and discussion

3.1 Ceramization process of the PMS- $TiCl_4$ precursors

After evaporation of toluene from the starting materials, a highly viscous and homogeneous mixture was obtained from 10% PMS- $TiCl_4$ precursor with an orange color. For a $TiCl_4$ content of more than 10%, the precursors were solidified during the solvent evaporation. After complete drying, a deep orange colored powder was obtained. Most of the mixtures and the original PMS were highly flammable in air. The PMS- $TiCl_4$ 10% mixture was, however, relatively stable, and did not ignite under atmospheric conditions.

After heat treatment at 723 K, the original PMS was transformed to a light orange solid, while the 10, 30, 40, 50%

Fig. 1. IR spectra of the PMS- $TiCl_4$ precursors.

Fig. 2. IR spectra of the PMS- $TiCl_4$ precursors heated at 523 K.

PMS- $TiCl_4$ samples became black solids, whereas the 60 and 75% PMS- $TiCl_4$ samples showed a deep purple color. The 60 and 75% PMS- $TiCl_4$ samples were found to be highly flammable under atmospheric conditions, even after heat treatment at 723 K.

Figure 1 shows IR spectra of the dried PMS- $TiCl_4$ samples. Broad absorption in the vicinity of 900-500 cm^{-1} may reveal the existence of an inorganic network, such as Si-Ti-C. There is, however, no marked difference in the intensity of the Si-H absorption (2100 cm^{-1}). The Ti molar ratio is considered to be small to diminish the intensity of the Si-H absorption. In the 40% and 50% PMS- $TiCl_4$ samples, broad absorption at 3300 and 1650 cm^{-1} were observed. Partial hydrolysis of residual Ti-Cl by ambient moisture is suggested in these precursors for OH group introduction.

Figure 2 shows IR spectra of the 523 K heat-treated samples. In the PMS- $TiCl_4$ precursors, broad absorption beyond 1200 cm^{-1} overlaps the absorption bands of the organic groups. This may reveal the evolution of inorganic networks during the heat treatment. At high $TiCl_4$ content, the intensity of Si-H absorption showed a substantial decrease as compared with that of Si- CH_3 absorption.

Figure 3 shows the mass loss curves of the 723 K heat-treated precursors (PMS, 10, 40, and 75% PMS- $TiCl_4$) up to 1273 K under an Ar atmosphere. It was observed that the original PMS precursor shows a mass loss of about 6% at 1273 K. The residual mass at 1273 K decreases with $TiCl_4$ content. Even the 10% and 40% PMS- $TiCl_4$ precursors exhibit notable mass loss beyond 1073 K, possibly caused by Ti-Cl

Fig. 3. Mass loss curves of the PMS-TiCl₄ precursors in an Ar atmosphere.

Fig. 4. XRD patterns of the PMS-TiCl₄ precursors pyrolyzed at 973 K.

bond decomposition. The 75% PMS-TiCl₄ precursor shows sharp mass loss at 850 K. This possibly corresponds to the residual TiCl₄ substance in the precursor. The small mass loss at 373–473 K observed in the 40 and 75% PMS-TiCl₄ precursors probably corresponds to the decomposition of Ti-OH groups, which are formed by partial hydrolysis reaction of Ti-Cl bonds during handling out of the glove box.

Figures 4 and 5 show the XRD patterns of the PMS-TiCl₄ precursors pyrolyzed at 973 and 1273 K, respectively. At 973 K, the sharp lines of TiSi₂ are clearly observed. The lines of SiC are, however, quite broad and show no indication of crystallite growth.

The PMS product (containing no Ti) shows broad SiC lines at 1273 K (Fig. 5). Besides the SiC lines, the sharpened TiSi₂ lines are observed in the 10–50% PMS-TiCl₄ products. The lines of Ti₃Si₅ are also observed in the 75% PMS-TiCl₄ sample. The 10% and 30% PMS-TiCl₄ samples, however, show the sharp line of the metallic silicon phase at 1273 K in addition to the TiSi₂ lines, unlike the XRD pattern of the PMS sample. It is not appropriate to assign the lines at 36, 59, and 70° in the 10% and 30% PMS-TiCl₄ samples for TiC, because the intensity of these lines is monotonously weakened as the TiCl₄ content increases.

The chemical reaction between the Si-H bonds and the Ti-Cl bonds at rather low temperature may explain the TiSi₂-

Fig. 5. XRD patterns of the PMS-TiCl₄ precursors pyrolyzed at 1273 K.

Fig. 6. XRD patterns of the PMS-TiCl₄ precursors pyrolyzed at 1573 K (in a graphite crucible).

like domain formation. Strong Ti-Si bonds may accelerate cleavage of Si-CH₃ to eliminate methane from the whole system during pyrolysis; a possible reason for the metallic silicon phase formation at 1273 K, and the absence of Ti₃SiC₂ phase.²⁰⁾ It is known that the bond energy of the Si-Si bond is lower than that of the Si-C bond, and thus atomic migration will be accelerated in a silicon rich network that pushes forward segregation and crystallization of TiSi₂, SiC, and metallic silicon.

Figure 6 shows the XRD patterns of the PMS-TiCl₄ products pyrolyzed at 1573 K in a graphite crucible. After pyrolysis, lines of metallic silicon are observed in PMS, 10 and 30% PMS-TiCl₄ samples in spite of the carbon rich atmosphere in the graphite crucible. In these XRD patterns, sharp SiC and TiSi₂ lines are also observed. In the 40 and 50% PMS-TiCl₄ samples, the SiC lines are split. This is due to TiC formation with the consumption of TiSi₂.

Most of the PMS-TiCl₄ precursors, except the 10% PMS-TiCl₄ sample, show a powder-like appearance after solvent removal. Even during pyrolysis at high temperature, there was no indication of fusing. Thus, the 10% PMS-TiCl₄ precursor is most promising for a wide range of applications from the viewpoint of its processability. The low carbon content expected from TiSi₂ and metallic silicon phase formation at low tem-

Fig. 7. Si and Ti mappings on the polished cross-section of the PMS-TiCl₄ 10% product at 1273 K.

Fig. 8. XRD patterns of the PMS-MoCl₅ 60% precursor pyrolyzed at various temperatures.

perature is also unique. On the other hand, the large amount of the TiCl₄ addition probably introduces a large number of cross-linking points in the starting PMS precursor to thwart its processable nature.

In order to investigate the homogeneity of the PMS-TiCl₄ 10% sample, a piece of the pyrolysis product was polished down to obtain element (Si and Ti) mappings of the cross-section (Fig. 7). It was observed that the distribution of silicon and titanium was not completely homogeneous. An undulating texture of 10–20 μm was observed on the Si and Ti mappings. These patterns may correspond to the phase separation patterns in the starting polymers. PMS densely cross-linked by TiCl₄ is possibly segregated from relatively low molecular weight PMS, which is not sufficiently cross-linked with TiCl₄. The segregation process in such a system, however, does not proceed completely to form independent domains because the cross-linking points intrinsically retard any kind of diffusion process.

3.2 Ceramization process of the PMS-MoCl₅ precursors

After evaporation of toluene from the starting solutions, PMS-MoCl₅ mixtures were obtained in the form of a black liquid. After heat treatment at 723 K, these black liquids were converted to black solids.

Figure 8 shows the XRD patterns of 60% PMS-MoCl₅ samples heat treated at various temperatures beyond 723 K. In the low temperature region of 1073 K, traces of β-MoSi₂ lines have already been observed. From 1173 K to 1273 K, these β-MoSi₂ lines disappear with the appearance of α-MoSi₂ lines. In the same temperature region, broad SiC lines are also observed. The metallic silicon phase is absent up to 1273 K.

Figure 9 shows the XRD patterns of the pyrolysis products of PMS-MoCl₅ precursors at 1273 K with the various MoCl₅ contents. At a low MoCl₅ content of 20 mass%, lines of α-

Fig. 9. XRD patterns of the PMS-MoCl₅ precursors pyrolyzed at 1273 K.

Fig. 10. Si and Mo mappings of the polished cross-section of the PMS-MoCl₅ 30% product at 1273 K.

MoSi₂ phase are observed. As the MoCl₅ content in the starting mixture increases, the line intensity of the α-MoSi₂ phase shows a small increase.

After heat treatment at 1773 K in a graphite crucible, the 20% PMS-MoCl₅ showed the line assigned to metallic silicon (28°). Its intensity was, however, quite low, which was different from the cases of the PMS-TiCl₄ precursors. As the MoCl₅ content in the starting mixture increased, the lines assigned to α-MoSi₂ increased with the decrease of the β-SiC lines. In spite of the carbon rich atmosphere during pyrolysis, Mo₂C phase was not formed. The α-MoSi₂ phase was sufficiently stable and the system did not contain metallic Mo.

Figure 10(a) shows elemental mappings of the cross-section of the pyrolysis product at 1273 K derived from the PMS-30% MoCl₅ precursor. Mo rich domains with irregular sizes were dispersed in the silicon rich domains. Elemental analysis of the dispersed domains generally indicated a composition of SiC and MoSi₂. On the other hand, the composition of the matrix area was consistent with silicon rich SiC. The obtained results indicate that the Mo rich domains always contain a considerable amount of SiC, while the matrix area contained almost no Mo.

Such a microstructure, however, was influenced by the solvent and additives used for the precursor preparation. As an example, the microstructure of the pyrolysis product of PMS-20%MoCl₅ precursor prepared with a large amount of THF (tetrahydrofuran)^{21),29)} is shown in Fig. 11. The Mo rich domain shows a spherical or droplet shape, which consists of small Mo rich particles. The Mo rich particles and the Si rich matrix form a complex interface in the observed droplets. In Fig. 11, we can observe the removal of one small Mo rich particle from the droplet isolated in the matrix.

XRD measurements on the PMS-MoCl₅ pyrolysis products indicated the existence of a high temperature, hexagonal β-

Fig. 11. Si and Mo mappings of the polished cross-section of the PMS-MoCl₅ 30% product at 1273 K. A 10-times mass of tetrahydrofuran is used for the MoCl₅ dissolution in the starting mixture.

MoSi₂ phase formation in quite a low temperature region. Such β -MoSi₂ phase formation at low temperature has been reported in cases of mechanical millings of Mo and Si powders.³⁰⁾ In our case, it is probable that the strong chemical interaction between PMS and MoCl₅ forms Si-Mo bonds during mixing, which are then converted to a molybdenum silicide-like structure during pyrolysis.

The observed microstructure at 1273 K is quite different from the microstructure of the PMS-TiCl₄ products. This difference is possibly caused by the valance of the MoCl₅, the solubility of the used solvent, and the interaction between PMS and MoCl₅. This issue, however, requires further investigation. The polarity of the used solvent and the types of additives for PMS cross-links will be major factors.

4. Summary

TiCl₄ added in PMS possibly reacts with almost all the PMS networks to yield Si-Ti bonds. The TiSi₂ phase is formed at 973 K. TiSi₂, SiC and Si phase crystallization at 1273 K is accelerated with the TiCl₄ addition. At a high TiCl₄ content beyond 50%, Ti₃Si₅ phase is formed, which is easily converted to TiC at 1573 K (in a carbon rich atmosphere). From the TiCl₄ content of 30%, the powdery precursor is obtained after solvent removal. Therefore, 0–10 mass% of TiCl₄ is considered to be appropriate to modify PMS from the viewpoint of processability.

MoCl₅ added in PMS also reacts with PMS to form Si-Mo bonds, which are converted to SiC-MoSi₂ domains during pyrolysis. Formation of β -MoSi₂ phase at 1073 K, which usually appears as a high temperature stable phase, also suggests the strong chemical interaction between Si and Mo. The conversion process of β -MoSi₂ to α -MoSi₂ crystalline phase proceeds at 1273 K. The microstructure of the obtained ceramics, however, depends upon the types of solvent used for the precursor mixing.

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