FUNDAMENTALS OF POLYMER PRECURSOR METHOD FOR SYNTHESIZING SILICON CARBIDE BASED CERAMIC FIBERS

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Inorganic fibers become major materials in modern industry. In particular, the carbon fiber technology shows remarkable development. Nowadays, carbon fibers with extreme strength and flexibility play an important role in airplane industry as carbon fiber reinforced plastic matrix composites (CFRP). Success of carbon fiber gives a clue that even the materials with no fusibility or with high melting points can be shaped to thin fiber form by using polymers as starting precursors.

In a decade of 1970s, Yajima evidenced that thin continuous SiC based fibers can be obtained from a kind of organosilicon polymers. This polymer, PCS, was synthesized by thermal condensation reaction of polydimethylsilane (PDMS). PDMS is intrinsically infusible and not soluble to any kinds of organic solvents because of the symmetric backbone structure. During the thermal condensation, chain scissions and recombination process introduce Si-CH_2-Si bridges and Si-H side groups in the polymer structure, which is called Kumada rearrangement process. PCS, thus obtained, is stable at a room temperature in an oxidation or humid atmosphere. The introduced Si-H side groups play an important role in curing process, which is necessary to make spun fiber infusible during the successive pyrolysis process. It should be paid attention that chemical composition of the PCS is not equal to the original PDMS. C/Si and H/Si molar ratios of PCS (1.87 and 4.55, respectively) is apparently lower than those of PDMS. It means that backbone of PCS possesses ladder-like or locally cross-linked structure. Relatively high softening point of PCS also suggests the existence of such rigid structure. Most of “polycarbosilane”, synthesized by synthetic chemistry is viscous liquid at room temperature. It is unfortunate that thermal condensation reaction of PDMS is mainly accompanied by evolution of gaseous silanes with monomethyl or dimethyl chemical groups, while evolution of methane and hydrogen is minor. Because of a large amount of such “silanes” removal, PCS yield from PDMS is known to be limited in the range of 60-65 mass%.

Melt spinnability is an essential issue in applying the polymer precursors for ceramic fiber technology. “Spinability” is however, rather a pragmatic term and the assessment is not easy. Evaluation of PCS melt viscosity suggested that the viscosity range of 5-10 Pa·s was appropriate for the fiber spinning. From the temperature dependence, the apparent activation energy of 180 kJ mol^{-1} was estimated for PCS, and addition of the plasticizer seemed to decrease the activation energy. By adjusting the plasticizer combination, thinner precursor fiber or the fiber with unique - controlled morphology was synthesized

The C/Si ratio of PCS exceeds 1.0, and thermal oxidation curing, adopted in early days, introduces a considerable amount of oxygen in the system. Thus, the classic SiC based fibers were generally amorphous with chemical compositions of Si-C-O or Si-C-O-M (M: metal). Development of ceramic-matrix composites (CMC), however, began to require maintenance of the fiber performance even at high temperatures beyond 1600 C. Near stoichiometric and more crystalline SiC fibers were developed in recent years in order to respond such market demands. One is Hi-Nicalon-Type S (NGS Advanced Fibers Co., Ltd), which uses electron beam curing and hydrogen decarboinization for adjusting the fiber chemical composition. Another is Tyranno SA (UBE industries, Ltd.), which becomes stoichiometric SiC via carbothermal reduction process. Existence of Al is believed to be essential for homogeneous crystallization. The technology of these advanced fiber production, however, contains more complex factors than the cases of classic ceramic fibers because the process contains the step of the large volume-weight shrinkage influenced by surrounding an atmosphere. Deeper information about local composition change, bond rearrangements and nano-micro crystallization process will become necessary for precise control of the whole process.