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Quantitative study on structural evolutions and associated energetics in polysilazane-derived amorphous silicon carbonitride ceramics

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Abstract

Several important structural changes and their energetics during high-temperature annealing of polysilazane-derived amorphous silicon carbonitride ceramics were quantitatively studied. A ^{29}Si solid-state NMR study indicated that the structural transition in the Si-containing area can be described by an equilibrium reaction, $4SiCN_3 = SiC_4 + 3SiN_4$. The enthalpy and entropy for the reaction were calculated to be positive. Raman and electron paramagnetic resonance (EPR) studies revealed that the structural evolution within the free carbon area includes the graphitization of amorphous carbon and the lateral growth of nanographite, accompanied by a decrease in the point defect concentration. EPR results also suggested that the materials contain two kinds of point defects: carbon-dangling bonds at the edge and in the interior of the nanographite. It was found that the lateral growth of the nanographite followed a 2-D grain growth process, and that the decrease in the defect concentration was mainly due to the growth of the nanographite. The energetics of the structural changes was rationalized according to a simple structural model, and the effects of these changes on the stability of the materials were discussed.

Keywords: Polymer-derived ceramics; Structure evolution; Thermodynamics; Energetics; Nanodomain

1. Introduction

Amorphous Si-based ceramics, such as SiCN, SiCO, SiBCN and SiAlCN, synthesized by thermal decomposition of polymeric precursors (referred to as polymer-derived ceramics (PDCs)) have received extensive attention in recent decades [1]. Compared to polycrystalline ceramics prepared by sintering the corresponding powders, this new class of materials exhibits a set of unique and superior properties, such as excellent creep resistance [2–4], remarkable thermal stability [5], outstanding oxidation/corrosion resistance [6–9], high-temperature semiconducting behavior [10,11] and anomalously high piezoresistivity [12]. These properties, together with the direct chemical-to-ceramic processing, make the materials very promising for a wide range of applications, including high-temperature ceramic fibers, ceramic composites, microelectromechanical systems/microsensors for harsh environments, gas separation/absorption, and thermal protection coatings [13–18].

The unique properties, and thereby the applications, of PDCs result directly from their unusual structures. A variety of spectroscopic and microscopic techniques has been employed to investigate the structure of polymer-derived SiCN [19–25]. These efforts have revealed a large amount of useful information, which paint a fairly clear picture about the PDC-SiCN structure. While it strongly depends

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on the chemistry of the precursors and processing conditions [1,23,26], the structure of carbon-rich PDC-SiCN possesses several common features. First, all SiCN ceramics contain a silicon-containing area and a carbon area (referred to as free carbon). The silicon-containing area is amorphous, and comprises of SiN_4 and SiC_4 tetrahedra cores embedded in mix-bonded SiC_xN_{4-x} ($x = 1$, 2, 3) units. The mix-bonded SiC_xN_{4-x} tetrahedra have been found in polysilazane-derived SiCN ceramics, but not in polysilylcarbodiimide-derived SiCN ceramics. On the other hand, the free carbon area can be viewed as an assembly of many relatively ordered carbon nanoclusters with a fairly large number of defects. These phases are arranged into a unique heterogeneous amorphous nanodomain structure [27].

Upon annealing at higher temperatures, SiCN undergoes a series of structural evolutions, towards ordering and eventual crystallization. The structural evolutions can be roughly divided into two stages: structural rearrangement at relatively lower temperatures (<1440 °C) and large-scale crystallization and carbothermal reaction at higher temperatures. The low-temperature structural evolution is rather interesting since many of the aforementioned functional properties are related to this unique nanodomain structure. It was revealed that the bonding type and bonding ratio in SiCN remained unchanged during annealing between 1000 and 1400 °C [28], suggesting that there is no net interaction between the Si-containing phase(s) and the free carbon phase within this temperate range. Therefore, the low-temperature structural evolution can be analyzed by considering the changes in the Si-containing area and in the free-carbon phase separately. Of course, the changes in the interface between the Si-containing area and free carbon area are also expected to play a key role in determining many of the properties of SiCN. It was revealed that the major structural evolutions include the following changes: the demixing of the SiC_xN_{4-x} mixed bonds into SiN_4 and SiC_4, resulting in the shrinkage of the SiC_xN_{4-x} area and the coarsening of the SiN_4 and SiC_4 areas [23,26]; and the graphitization of the free carbon, accompanied by an increase in the order of the carbon nanoclusters and a decrease in the concentration of the defects [22,29,30].

Further important progress in the understanding of PDCs has come from the measurement of their energetics using high-temperature oxide melt solution calorimetric methods [31]. It was revealed that most of the reported SiOC, SiCN, SiCNO and SiBCN ceramics exhibited a negative heat of formation with respect to a mixture of their crystalline counterparts of the same composition [23,24,26]. Upon high-temperature annealing, the SiCN ceramics derived from polysilazanes showed a decrease in enthalpy [23].

In spite of these extensive studies, two aspects of the structural evolution of SiCN have received little attention. First, even though the variation of different phases with annealing temperature has been well documented, these previous studies primarily focused on showing the qualitative trend; no quantitative study on the structural evolution has been reported. Second, the previous calorimetric measurements can only provide energetic information on the entire material as whole; the energetics involved in each process of the structural evolution has not been reported. In this paper, we report a quantitative study on the structural evolution of a SiCN derived from polysilazane. Several important structural changes in both the Si-containing area and the free carbon area are quantified individually. The energetics involved in each of these changes are derived and discussed in terms of their role in determining the stability and evolution of the SiCN.

2. Experimental

The SiCN studied here was prepared by thermal decomposition of a commercially available polysilazane (HTT1800, Kion Corp., Columbus, OH, USA) [32]. The precursor was first solidified without any catalyst in a Teflon tube at 200 °C for 16 h under ultrahigh-purity argon (UHP Ar) protection. The obtained solid was then pyrolyzed under a steady flow of UHP Ar in a quartz tube furnace (GSL-1100X, MTI Corporation, Richmond, CA) using the following schedule: (i) heating to 900 °C at a heating rate of 3 °C min^{-1}, (ii) further heating to 1000 °C at a heating rate of 1 °C min^{-1}; (iii) keep at 1000 °C for 4 h; and (iv) cool to room temperature at a cooling rate of 5 °C min^{-1}. The obtained ceramic was further annealed at different temperatures up to 1350 °C for 4 h under UHP Ar protection in an alumina tube furnace (GSL-1600X, MTI Corporation, Richmond, CA). The resultant samples were analyzed using X-ray diffraction (XRD; Rigaku, Tokyo, Japan), which reveals that regardless of annealing temperature, all samples were amorphous. The polymer-to-ceramic conversion of the polysilazane was studied by thermogravimetric analysis (TGA; SDT Q600, TA Instruments, New Castle, DE) in UHP Ar atmosphere up to 1400 °C, using a heating rate of 5 °C min^{-1} and an argon flow rate of 150 ml min^{-1}.

The resultant ceramics were characterized using high-resolution solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) on a Bruker DRX spectrometer at a static magnetic field of 19.6 T (^1H frequency: 830 MHz). ^{29}Si solid-state NMR spectra were recorded at Larmor frequencies of 165.5 MHz. All spectra were acquired using a standard single-pulse sequence with a tip angle of ~45° and a recycle delay time of 5 s and based on a total of 2048 scans. The ^{29}Si chemical shifts were referenced to tetramethylsilane (TMS).

The materials were also characterized by Raman spectroscopy using a Renishaw inVia spectrometer (Renishaw Inc., Gloucestershire, UK), equipped with a 532 nm Si solid laser excitation source and a sensitive Peltier-cooled couple-charged device (CCD) detector. The laser beam was focused on the sample through a ×50 objective lens. The laser spot size was ~10 μm in diameter and the laser