NMR Study on Polymer Derived Ceramics

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Introduction

Polymer derived ceramics are a new class of multifunctional high-temperature materials synthesized by thermal decomposition of polymeric precursors [1,2]. The materials have a unique structure, which is neither amorphous nor crystalline. Instead, it contains Si-C-N disordered nanodomains and graphene/free carbon clusters. The structure is evolved with annealing temperatures, as indicated by significant change in their conductivities and thermal stabilities. Particularly, annealing-temperature dependent conductivity of the materials has gained significant recent attention due to their potential application in high-temperature MEMS and micro-sensors [3,4]. However, this phenomenon has not been fully understood. Better understanding of the phenomenon requires knowledge of the structural evolution of the materials with annealing temperature.

In this research, the structures of polymer-derived ceramics have been studied using solid-state NMR. The obtained results are used to get quantitative information about the structural evolution.

Experimental

The amorphous SiCN ceramics are obtained by thermal decomposition of a polysilazane at temperatures of 1100, 1200, 1300 and 1350°C for 4 hrs, respectively. The ^{29}Si-NMR solid state NMR experiments were performed on a 19.6 T magnet with a 830MHz Bruker DRX console and a NHMFL built 4mm MAS probe. The sample spinning rate was 8kHz. A 45° (3μs) pulse and 5 sec delay were used. The chemical shift is referenced to TMS (0ppm).

Results and Discussion

The obtained NMR spectra of the four SiCN samples are illustrated in Fig. 1(a). The curve-fitting of these spectra (Fig. 1(b)) reveals that all spectra contain 5 peaks, corresponding to SiO_2, SiO_2 in mullite, SiN_2O_2, $SiCN_3$ and SiC_2N_2. With increasing annealing temperature, the peaks become sharp with less overlap, suggesting the structure becomes less disordered and less phase separation.

The relative concentration of these units within the samples are calculated from the intensity of these peaks and listed in table 1. It is seen from the table that with increasing annealing temperature, the concentrations of SiO_2 and SiC_2N_2 are increased, while those of SiN_2O_2 and $SiCN_3$ are decreased. The temperature at which the sharp change in structural unit concentration occurred is ~ 1200-1300 ^{o}C. This is consistent with electrical conductivity measurement, which also showed that significant change occurred in this temperature range [5].

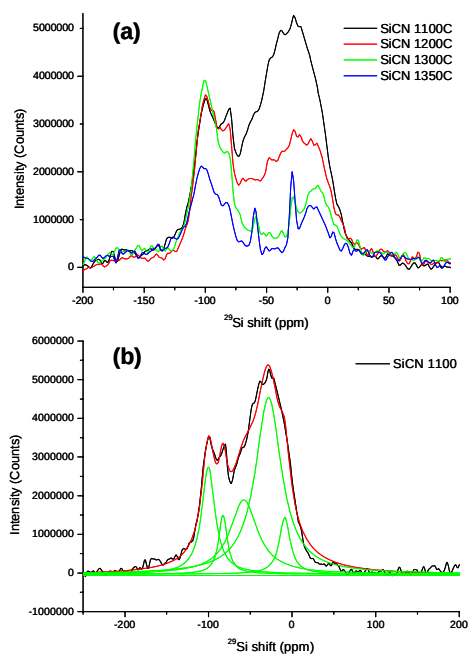

Fig. 1. ^{29}Si-NMR spectra of the SiCN samples.

Table 1: Concentrations of structural units as a function of annealing temperature.

	SiO_2	SiO_2(m)	SiN_2O_2	$SiCN_3$	SiC_2N_2
1100	15.5	5.5	22.2	50.2	6.6
1200	20.2	17.7	30.5	11.5	20.0
1300	47.6	19.8	1.2	2.6	28.8
1400	53.7	7.3	3.3	7.0	28.7

References

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