NMR STUDIES ON STRUCTURES OF POLYMER-DERIVED AMORPHOUS SiAlCN CERAMICS AND STRUCTURES OF OXIDE LAYER THERMALLY FORMED ON THE SiAlCN

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Introduction

Polymer-derived ceramics, in which silicon-based ceramics are synthesized by thermal decomposition of polymeric precursor, are a new class of materials that have attracted extensive attention in the last decade. The obtained materials are amorphous alloys consisting of Si, C and N, and the forth elements such as B, Al and etc. can be incorporated into the network to modify the structure and thereby the properties. Our recent research [1] revealed that the amorphous SiAlCN possess unique properties: (i) high oxidation and hot-corrosion resistance than any other Si-Based materials and (ii) high electric conductivity and the conductivity increase with annealing temperatures. We have applied multi-nuclei (^{29}Si and ^{27}Al) solid-state NMR to study the structures of the oxide scale thermally formed by oxidation of the SiAlCN.

Experimental

Three SiCN samples that have different compositions and electric conductivity behaviors were prepared at UCF, SiCN ($SiC_{0.99}N_{0.85}$), SiAlCN-5, ($SiAl_{0.02}C_{0.84}N_{0.90}$) and SiAlCN-5 $SiAl_{0.04}C_{0.83}N_{0.93}$. Low field NMR experiments (7.4T) have been performed at PNNL and we present here our first experiment with higher magnetic field (19.6T) which gives much higher sensitivity.

Results and Discussion

Figure 1 shows the ^{29}Si NMR spectra acquired at 19.6T. The broader peak consists of ^{29}Si signals with various coordination numbers that are partially overlapped for the disordered system. The spectra show the changes of relative intensities for the three samples. Together with the lower field results (not shown) with various annealing temperature and time, we are able to measure the oxide scale in terms of oxidation temperatures, annealing time and aluminum-content. These results help us to understand two important findings: the lower oxidation rate and the decrease in oxidation with annealing time in SiAlCN samples. The lower oxidation rate is attributed to the unique network structure of the oxide scale in which Al atoms sit in the center of 6-membered Si-O rings to block oxygen diffusion. Such a unique structure was likely formed gradually with annealing time, leading to the continuous decrease in oxidation rate. A paper has been submitted to Journal of the American Ceramic Society [2].

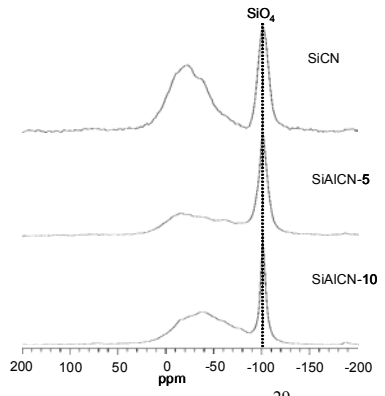

Figure 1. Comparison of ^{29}Si NMR spectra for different SiCN samples.

References

[1] An, L., *et al*., *Adv. Eng. Mat*., 6[5], 337-40 (2004).
[2] Wang, Y., *et al*., *J. Am. Ceram. Soc.*, submitted (Dec. 2004).