

Polymer-Derived Ceramics Investigated by Means of Pair Distribution Function from Electron Diffraction in TEM

Stefania Hapis¹, Hans-Joachim Kleebe¹, Yan Gao², Ralf Riedel², Jochen Rohrer², Xiaoke Mu^{3/4}, Peter van Aken³

¹ Technische Universität Darmstadt, Institut für Angewandte Geowissenschaften, Darmstadt, Germany

² Technische Universität Darmstadt, Institut für Materialwissenschaft, Darmstadt, Germany

³ Max-Planck Institute für Intelligente Systeme, Stuttgart Center for Electron Microscopy, Stuttgart, Germany

⁴ University of Strasbourg/ CNRS, Institute for Physics and Chemistry de Physique et Chimie des Matériaux, France

For the last decades Polymer-Derived Ceramics (PDC) were studied due to their outstanding properties, e.g. high strength, high creep, oxidation and corrosion resistance and stability against crystallization as well as decomposition [1]. Therefore, these ceramics are promising materials for widespread applications, including high strength fibers, coatings, ignition plugs, MEMS devices, as well as anode materials for lithium-ion batteries [2]. These properties are attributed to a unique microstructure of the PDCs, which can only be obtained by thermolyzing polymeric precursors. The compositions of the ceramics can be tailored by changing the architecture and chemistry of the used precursor. But the microstructure and their crystallization behavior in the amorphous ceramics (up to 1400°C) are still not completely understood.

The Pair Distribution Function (PDF) is a powerful technique to investigate the short range order (SRO) in already established for example in X-ray or neutron diffraction but the advantage of the PDF from electron diffraction is that a very small sample volume can be analyzed in conjunction with the corresponding image information (HRTEM). Therefore, the analysis of the SRO in these amorphous PDC ceramics is carried out by means of PDF from electron diffraction in the TEM.

The microstructures of the polymer-derived ceramics are strongly dependent on the material system, the characteristics of the used precursors, and the processing conditions [3-5]. The PDF technique is used for a better understanding of the crystallization behavior of these ceramics. By now, it is known that the onset of crystallization in boron-containing ceramics is shifted towards higher temperatures; While a high amount of carbon inhibits the formation of nanodomains in the system, even small boron contents influence remarkably the resulting microstructure in the final ceramic as it can be seen in Figure 1 a,b. Likewise, the bonding distances in the amorphous ceramic at 1400°C, shown with the Pair Distribution Function (Fig. 1c), reveal to be shorter in the boron-containing counterpart. The relationship between the molecular architecture and chemistry on the amorphous nature of the pre-ceramic and, in addition, its influence on the resulting crystallization behavior will be discussed.

For a proper analysis a calculated structure of the possible atomic arrangement is needed to be compared with the experimental data. Therefore, the simulated structure model has to be used to calculate a kinematical diffraction profile so that all related parameters from the experiment can be taken into account. It should be noted that the experimental PDF are compared to calculated PDFs obtained from structure models by Density Functional Theory (DFT) simulation.

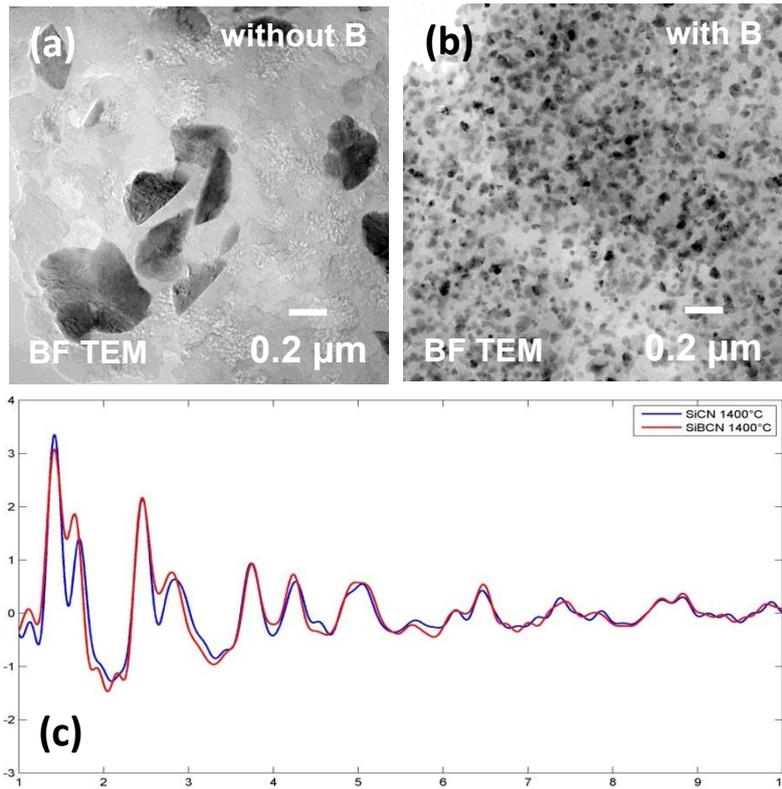


Figure 1. a) BF TEM micrograph of the SiCN ceramic annealed at 1700°C; b) BF TEM micrograph of the SiBCN ceramic annealed at 1700°C, in comparison it is obvious that the resulting crystal-size differs significantly only by adding 3 wt.% boron; c) the resulting Pair Distribution Function from SiCN and SiBCN ceramics annealed at 1400°C already shows shorter bonding distances.

References:

[1] P Colombo et al, *J Am Ceram Soc*, **93** (2010), pp. 1805-1837.
 [2] P Colombo in “Polymer derived ceramics: from nanostructure to applications”, ed. P Colombo, R Riedel, GD Sorarú and HJ Kleebe, (DEStech Publications Inc., Lancaster) (2009).
 [3] G Mera et al, *J Am Ceram Soc*, **93** (2010), pp. 1169-1175.
 [4] A Saha et al, *J Am Ceram Soc*, **88** (2005), pp. 232-234.
 [5] A Saha et al, *J Am Ceram Soc*, **89** (2006), pp. 2188-2195.
 [6] The author acknowledges funding of the German Research Society (DFG) for the Project ‘Nanostructure and Calorimetry of Amorphous SiCN and SiBCN Ceramics’. As well, financial travel support of the Woman’s Representatives from the Department 11 of the Technical University is gratefully appreciated.