Effect of Carrier Gas on the Conversion Process of BN Organic Polymer Precursor to BN Ceramic

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Abstract: Boron nitride organic polymer precursors were pyrolyzed under different carrier gases such as NH₃, Ar and N₂. The conversion process of BN organic polymer precursor to BN ceramic was characterized by means of TG, FTIR, and elemental analysis. Results showed that NH₃ could promote conversion process which was beneficial to the occurrence of hydrolysis, crosslinking and decomposition reaction. Therefore, lower carbon residue existed and more regular inorganic structure were obtained in boron nitride precursor pyrolytic products which would be helpful to gain BN fiber with excellent wave transparent properties.

1. Introduction

Boron nitride (BN) fiber occupied many excellent physical and chemical properties such as high temperature resistance, chemical corrosion resistance, excellent dielectric properties and good thermal conductivity. More importantly, BN fiber could keep almost constant in strength at 2000°C in inert atmosphere and stable in chemistry and structure below 850°C, which could be used as high temperature wave transmitting components in aerospace and nuclear industry fields due to the excellent heat resistant, wave dielectrical and ablation resistant properties [1-6]. One of the most common preparation methods for BN fibers is to use organic polymer precursor derived from B-tri(alkylamino)borazines, such as tri(methylamino)borazine ([CH₃(H)N]₃B₃N₃H₃). The method mentioned above possessed typical characteristics of high molecular designability and structural controllability which is helpful to gain high crystallinity and good mechanical properties for BN fibers. The conversion process of BN organic polymer precursor to BN ceramic (polymer-to-ceramic conversion process) was the most important phase for the preparation of BN fibers. The small molecule gas escaped continuously from the polymer precursor and organic compounds were gradually transformed into inorganic compounds during the conversion process.

It was generally appreciated that carrier gases affected the removal process of carbon residue obviously which was the key influencing factor in the dielectric properties and the oxidation resistance of the wave transparent materials. Therefore, it was of great significance to study decarburization mechanism of carrier gases. In this work, the polymer-to-ceramic conversion process was researched, and the function of carrier gases was studied in detail which would provide material and technical support for the preparation of high performance BN fibers [7-9].
2. Experiment

2.1. Preparation of BN organic polymer precursor
Boron nitride organic polymer precursor was derived from the polymerization of tri(methylamino)borazine ([CH₃(H)N]₃B₃N₃H₃) which was obtained by the substitution reaction of chlorine atoms of B-tri(chloro)borazine (Cl₃B₃N₃H₃) by methylamine (CH₃NH₂).

[CH₃(H)N]₃B₃N₃H₃ and Cl₃B₃N₃H₃ were moisture-sensitive. So all the chemical reaction mentioned above were carried out under atmosphere of Ar atmosphere according to Schlenk techniques.

2.2. The polymer-to-ceramic conversion process
BN organic polymer precursor was placed in a quartz tube furnace and pyrolyzed at different temperatures from room temperature to 1000°C and under different carrier gases such as NH₃, Ar and N₂. Other process parameters remained the same with heating rate of 2°C/minute and dwell time of 2 hours. Then the pyrolytic products were obtained under different temperatures and carrier gases for further research.

2.3. Detection and characterization
The polymer-to-ceramic conversion process was investigated through the thermogravimetric (TG). The chemical bonds and functional groups of the pyrolytic products were analyzed on Fourier transform infrared spectroscopy (FTIR). Then, the element contents were measured through energy dispersive X-ray spectroscopy.

3. Results and Discussion

3.1. Pyrolysis process analysis of BN polymer precursors
In this study, BN polymer precursors were pyrolyzed in a quartz tube furnace up to 1000°C with heating rate of 2°C/minute and dwell time of 2 hours under NH₃, Ar and N₂. Then the thermogravimetric (TG) curves were obtained shown in Figure 1.

Results showed that the thermogravimetric curves were similar for the pyrolysis process of BN polymer precursor under Ar and N₂. The weight changed slightly with the weight loss less than 4.00%.

![Figure 1. TG curve of BN polymer precursor under NH₃, Ar and N₂.](image-url)
wt% from room temperature to 200°C, and the weight loss increased to 59.8 wt% and 57.5 wt% at 1000°C under Ar and N₂ respectively. When the BN polymer precursor was pyrolyzed under NH₃ atmosphere, the weight loss reached 23.03 wt% from room temperature to 200°C which was apparently higher than that under Ar and N₂. Moreover, the ultima weight loss reached 62.71 wt% at 1000°C which was also obviously higher than that under other carrier gases. That is to say, NH₃ could effectively promote the initiation of pyrolysis process and lead to more thorough escape of small molecules which might help to the preparation of BN fibers with lower carbon residue.

3.2. FTIR and elemental analysis of pyrolytic products

FTIR analysis was carried out for the further study of molecular structure and composition during the polymer-to-ceramic conversion process. The FTIR curves of pyrolytic products under N₂ and Ar atmosphere were shown in Figure 2 and Figure 3 respectively.

When the BN polymer precursor was pyrolyzed at 400°C, there were a large number of absorption peaks in the range of 1000~1500cm⁻¹ and 2800~3000 cm⁻¹. It was worthwhile to note absorption peaks at 1080cm⁻¹ and 2900cm⁻¹ were assigned to be the C-N and -CH₃ characteristic stretching bonds which meant the existence of carbon residue. When the pyrolysis temperature increased to 1000°C, the absorption peaks mentioned above disappeared generally and the polymer-to-ceramic conversion process was basically completed. Previous studies had shown that the absorption peak at 800cm⁻¹ represented the existence of BN six membered ring structures. According to the FTIR spectra shown in Figure 2 and Figure 3, the weak signal at 800cm⁻¹ suggested that only a part of B and N atoms took part in inorganic process and less six membered ring structures existed in the pyrolytic products [10-13]. That is to say, the polymer-to-ceramic conversion process mainly relied primarily on the crosslinking and decomposition reaction between active groups in the polymer instead of the participation of N₂ and Ar, which might be unfavorable for the removal of carbon and hydrogen elements. The relationships of element contents and pyrolysis temperature under N₂ and Ar atmospheres were shown in Figure 3 and Figure 4. Results showed that the carbon and hydrogen contents decreased with the increase of pyrolysis temperature. When the pyrolysis temperature increased to 1000°C, the carbon and hydrogen residue contents dropped to 8.94 wt% and 1.12 wt% under N₂ atmospheres and dropped to 9.67 wt% and 1.35 wt% under Ar atmospheres respectively.

In summary, a large number of organic components were retained in the pyrolytic products in the form of carbon residue which affected the dielectric properties of BN fiber seriously. Therefore, removal of carbon residue might become the key to obtain BN fiber with excellent wave transparent properties.

![Figure 2. FTIR spectra of pyrolytic products at various temperatures in N₂ atmosphere.](image-url)
Figure 3. FTIR spectra of pyrolytic products in Ar atmosphere.

Figure 4. Carbon residue in the pyrolyzed precursors under N$_2$ and Ar atmosphere.

Figure 5. Hydrogen residue in the pyrolytic precursors under N$_2$ and Ar atmosphere.
The FTIR curves of pyrolytic products under NH$_3$ atmosphere were shown in Figure 6. When the BN polymer precursor was pyrolyzed at 400°C, the C-N characteristic absorption peak at 1080 cm$^{-1}$ almost disappeared and the C-H characteristic absorption peak at 2900 cm$^{-1}$ became distinctly weaker which meant most of the organic groups were removed in the form of small molecule gases under the participation and action of NH$_3$ [11]. When the pyrolysis temperature reached 600°C, only characteristic absorption peaks of BN six membered ring structures at 800 cm$^{-1}$, B-N bonds at 1360 cm$^{-1}$ and N-H bonds at 3430 cm$^{-1}$ were detected in FTIR spectra. It could be deduced that the organic components were removed almost completely at 600°C under NH$_3$ atmosphere [13,14].

![Figure 6. FTIR spectra of pyrolytic products at different temperature in NH$_3$ atmosphere.](image1)

![Figure 7. FTIR spectra of pyrolytic products at different atmosphere.](image2)

FTIR spectra of pyrolytic products at 1000°C under N$_2$, Ar and NH$_3$ atmosphere were analyzed individually in order to describe the structural differences more clearly shown in Figure 7. Experimental results indicated that the characteristic absorption peaks of BN six membered ring...
structures at 800cm$^{-1}$ was the strongest in the pyrolytic products under NH$_3$ atmosphere. According to the element analysis of carbon residue in the pyrolytic products under NH$_3$ atmosphere, the carbon residue contents dropped to 0.45 wt% at 1000$^\circ$C which was obviously lower than that under N$_2$ and Ar atmospheres (Figure 8). Furthermore, only traces of hydrogen residue could be found with the test value lower than 0.1wt%.

Consequently, it was concluded that carbon and hydrogen residues could be removed more completely under NH$_3$ than that under N$_2$ and Ar atmospheres.

![Figure 8. Carbon elements residue in the pyrolytic products under NH$_3$ atmosphere.](image_url)

3.3. Reaction mechanism of NH$_3$ atmosphere during polymer-to-ceramic conversion process

Based on the research mentioned above, (NH$_2$)B- with high reactivity and CH$_3$NH$_2$ gas were generated which was attributed to the reaction of NH$_3$ and -NHCH$_3$ group. -CH$_3$ group in -(NH)CH$_3$ was substituted by -NH$_2$ in (NH$_2$)B- group shown Figure 9. Both of the reactions favored the reduction of carbon element and the formation of BN six membered ring structures which might help to the preparation of BN fiber with lower carbon residue [15]. The reaction mechanism of NH$_3$ carrier gas during polymer-to-ceramic conversion process would studied deeply in the future research.

![Figure 9. Chemical reactions of NH$_3$ during the polymer-to-ceramic conversion process.](image_url)
4. Conclusion
Boron nitride was prepared through pyrolysis reaction from boron nitride polymer precursor under different carrier gases. NH3 could promote inorganic process of boron nitride polymer precursor, and lower carbon residue existed and more regular inorganic structure could be obtained in boron nitride ceramic.

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