Nano-Structured Si/C/N Composite Powder Produced by Radio Frequency Induction Plasma and its Microwave Absorbing Properties

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Abstract

Nano-structured Si/C/N composite powders were produced by radio frequency (RF) induction plasma utilizing methyltrichlorosilane (CH\textsubscript{3}SiCl\textsubscript{3}) and nitrogen (N\textsubscript{2}) as precursors. The micro-morphology, chemical composition, functional group structure and absorbing properties of the samples were investigated. The results indicate that the size of Si/C/N particles is 0-50 nm with homogeneous distribution. The Si/C/N composites mainly consist of SiC (40.97\%) and Si\textsubscript{3}N\textsubscript{4} (51.03\%). The Fourier transform infrared (FT-IR) spectroscopy characterization shows that the composites have stronger Si-C (780 cm\textsuperscript{-1}) and Si-N (950 cm\textsuperscript{-1}) absorbing bands. Moreover, the composites possess good microwave absorbing properties.

Keywords: Si/C/N, Nanocomposite powder, Radio frequency plasma, Absorbing properties

1. Introduction

Absorbing materials play an important role in military and civil application. Progress in the engineering of antennas and electromagnetic shielding systems depends crucially on the development of materials absorbing electromagnetic radiation in a broad range, from meter to millimeter waves\textsuperscript{[1,2]}. The high absorbance of such materials must be combined with low reflectance in the same frequency range\textsuperscript{[3]}

Various kinds of materials can be used for absorbing materials, including metal-alloys\textsuperscript{[4-6]}, ceramic, oxides, composites and transition metal sulfide absorbing materials. Nano-structured absorbing materials have received steadily growing interest because of their fascinating properties like wide absorbing frequency, low density and good compatibility, compared with the bulk or microsized counterparts. The increased surface area, number of dangling bond atoms and unsaturated co-ordination on surface leads to interface polarization, multiple scatter and absorbing more microwave\textsuperscript{[7] [8]}. It is proposed that the nano-structured composite absorbing materials are the future research tendency of absorbing materials.

There are many methods for nano-structured materials preparation, among which thermal plasma is a novel technique. During the process, thermal plasma is normally generated by direct current (DC) arc or inductively coupled radio frequency (RF) discharge [9-11]. It can be described as a high enthalpy flame with extremely high temperature fields (10000-20000 \textdegree\text{C}) and a wide range of velocity fields from several m/s to supersonic values. Since the resultant huge enthalpy can be realized for various kinds of plasma forming gases and easily controlled by electricity, thermal plasmas have been expected to facilitate not only fast chemical reactions but also rapid heat transfer in a variety of synthetic routes for nano-structured materials.

Silicon carbide matrix composite would be a good candidate for microwave absorbing materials. Especially, it has been reported that Si/C/N and Si/C/N/O nano composites have good absorbing properties in the wave range of centimeters to millimeters\textsuperscript{[12-14]}. However, there are few reports on the preparation of nano-structured Si/C/N composite powders by RF technique. Therefore, this work is aimed at exploring the feasibility of produce nano-structured Si/C/N powders by RF plasma. Moreover, the microwave absorbing properties were investigated.

2. Experimental

The nano-structured Si/C/N composite powder was synthesized from methyltrichlorosilane (CH\textsubscript{3}SiCl\textsubscript{3}, 99.0\% purity), nitrogen (N\textsubscript{2}, 99.999\% purity) and hydrogen (H\textsubscript{2}, 99.999\% purity) in a RF torch system. The reactant gas composition was optimized by adjusting the amounts of CH\textsubscript{3}SiCl\textsubscript{3}, H\textsubscript{2} and N\textsubscript{2}. The temperature of the RF plasma reactor was detected by a pyrometer and the temperature was maintained at 3600-4800\textdegree\text{C}.

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Scattering electron microscope (SEM) was taken to investigate the micro-morphology of the nano-structured Si/C/N composite powders prepared by RF plasma. The images were observed under an acceleration voltage of 5.0kV with a HITACHI S-4300 scanning electron microscope. The chemical composition of the Si/C/N composite powder was determined with a nitrogen analyzer (LECO-TN114) for the nitrogen content, with an oxygen analyzer (LECO-RO316) for the oxygen content, and with a carbon analyzer (LECO-CS334) for the carbon content. The silicon content was calculated as the remaining. Surface functional groups of the sample are investigated by Fourier transform infrared (FT-IR) spectroscopy system (Thermo Scientific Nicolet 6700, America). The microwave absorbing property of the nano-structured Si/C/N composites within the frequency range of 8.2–12.4 GHz was investigated utilizing Agilent 8722ES microwave vector network analyzer.

3. Results and discussions

The SEM micrograph of the Si/C/N composites powders is shown in Fig.2. From Fig.2, it can be seen that most of the Si/C/N particles produced by RF plasma are in the size of ~50nm. The size of these particles is relatively uniform, but there is some agglomeration. During the RF plasma process, the temperature is very high and the nano-structured particles have higher surface energy, which would result in the agglomerations.

For absorbing materials, the composition plays the most important role on the absorbing properties. The chemical composition of the Si/C/N powders is shown in Table 2.

Table 2 The chemical composition of the Si/C/N powders

| Element | wt.% |
|---------|------|
| Si      | 58.98|
| C       | 14.82|
| Cf      | 6.55 |
| N       | 19.91|
| O       | 0.16 |

According to the composition, the chemical constituent of the composites can be calculated. It is simply assumed that the Nitrogen element is in the form of Si3N4, the Carbon element is in the forms of SiC and free carbon (Cf) and the Oxygen element is in the forms of SiO2 and adsorbed oxygen (O2) on the powder surface, respectively. Therefore, the calculated chemical constituent of the composites is listed in Table 3.

Table 3 The chemical constituent of the Si/C/N composites

| Constituent | wt.% |
|-------------|------|
| SiO2        | 0.30 |
| SiC         | 40.97|
| Si3N4       | 51.03|
| Cf          | 7.55 |
| O2          | 0.05 |

Factually, the Nitrogen element may be existed in a much more form. Some Nitrogen atom can dope in the lattice of SiC. In Si/C/N absorbing materials, some Carbon atoms in SiC are replaced by Nitrogen, resulting in negatively charged cavities. Under the electric field, the electromagnetic wave can be consumed by polarization relaxation of cavities[12]. For the reason, the strength of electromagnetic wave is weakened and the absorbance is enhanced.

Fig. 3 shows the FT-IR spectra of the Si/C/N powders. The corresponding functional groups have been marked in the figure. It indicates that the specimen have some functional groups, such as Si-O-Si, Si-N, Si-C, C-OH, Si-H, Si-CH3, C-O, C-H. These assignments were made based on...
the assignments and references reported by Zhou et. al [15]. The major difference between the FT-IR spectrums recorded in this work and that of Zhou et. al is the presence of the strong broad absorption band at 967 cm\(^{-1}\) peak found here. This band may be assigned to both Si-N and Si-C combined. The Si-C (780 cm\(^{-1}\)) and Si-N (950 cm\(^{-1}\)) bands in bulk are generally reported to be broad.

Based on the electromagnetic parameters of the Si/C/N composites, the relationship between reflection coefficient (X-band) and the thickness of the absorber can be simulated (see in Fig.4) by software named FLUENT 6.3. From Fig.4, it can be seen that with the increasing thickness of the absorber, the reflection coefficient is reduced obviously. Moreover, with the increasing frequency, the reflection coefficient is also reduced at the same thickness.

| Frequency/GHz | \(\varepsilon''\) | \(\mu''\) |
|---------------|-----------------|-------------------|
| 8.2           | 5.78            | 0.01              |
| 8.6           | 5.54            | 0.01              |
| 9.0           | 5.32            | 0.01              |
| 9.4           | 5.15            | 0.01              |
| 9.8           | 5.02            | 0.01              |
| 10.2          | 4.89            | 0.01              |
| 10.6          | 4.75            | 0.01              |

4. Conclusion

In summary, nano-structured Si/C/N composite powders were successfully produced by radio frequency (RF) induction plasma utilizing methyltrichlorosilane (CH\(_3\)SiCl\(_3\)) and nitrogen (N\(_2\)) as precursors. The micro-morphology, chemical composition, functional group structure and absorbing properties of the samples were investigated. The
results indicate that the size of Si/C/N particles is ~50 nm with homogeneous distribution. The Si/C/N composites mainly consist of SiC (40.97%) and Si$_3$N$_4$ (51.03%) and the composites have stronger Si-C (780 cm$^{-1}$) and Si-N (950 cm$^{-1}$) absorbing bands. Moreover, the composites possess good microwave absorbing properties.

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