Microstructure and mechanical properties of silicon carbide ceramics reinforced with multi-walled carbon nanotubes

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Abstract. A microstructure, a composition and mechanical properties of multi-walled carbon nanotube-reinforced silicon carbide ceramics were examined. The amount of carbon nanotubes was up to 1% wt. Samples was prepared by spark plasma sintering. It has been found that the optimal sintering temperature is 2000°C with an exposure duration of 5 minutes and a pressure of 50 MPa. The effect of the CNT mass fraction on the Young modulus of silicon carbide ceramics composites was investigated for different temperatures and processing conditions of samples using ultrasonic techniques. It has been established that Young’s modulus of ceramics decreases due to addition of CNT. Elastic properties of the composites cross section were characterized using nano-indentation. It has been revealed that the stiffness of the ceramics intergranular phase decreases due to addition of CNT.

1. Introduction

Composite ceramics reinforced with carbon nanoparticles is a new class of advanced materials for spacecraft engine elements [1, 2]. In this work, we will study the problem of production of composite ceramics based on silicon carbide and reinforced with multi-walled carbon nanotubes. The spark plasma sintering method is used to prepare samples. The purpose of the study is to improve mechanical properties of ceramics within a temperature range of up to 1200 °C.

It is known, that addition of carbon nanotubes may provide enhancement in strength and toughness of different types of ceramics [1-8]. A considerable number of SiC-CNT ceramics studies [3-8] have examined various sintering technologies including spark plasma sintering, precursor infiltration and pyrolysis, a hot-press method, etc. Bending strength of such composites is usually 200...400 MPa and fracture toughness is 2...7 MPa m⁰.⁵.

This work contains a study of the microstructure and the composition of SiC-CNT small samples. The relationship between the CNT volume fraction and Young modulus of silicon carbide ceramics composites was studied. It is noteworthy, that the elastic modulus value is directly included in the formula for calculation of fracture toughness by the indentation tests [9]. It should also be noted that the elastic modulus value considerably affects the results of the notched samples tests [10]. Therefore,
the reliable determination of composite ceramics Young’s modulus could provide an update of measured values of fracture toughness. Besides, the values of ceramics effective modulus and elasticity modulus of grains (measured by nano-indentation) enables the identification of important micromechanical parameters required for modeling of effective properties of ceramics composites [11].

2. Experimental procedure

Green silicon carbide powder (SiC) with an average size of particles of 5 µm and amorphous boron were used as basic material. Multi-walled carbon nanotubes with the following specification were used for reinforcement: the outside diameter is 50…80 nm, the inside diameter is 5…15 nm, the length is 10…25 µm, the specific surface area is 90…160 m²/g, density is 2.1 g/cm³. The composition is C – 97.32%, Cl – 0.21%, Fe – 0.56%, Ni – 1.88%, S – 0.03%.

For disaggregation and formation of a monodisperse system, multi-layer carbon nanotubes were dispersed using an ultrasonic unit during one hour. A polyvinyl alcohol 0.5% solution was used as dispersion medium; the ratio of the number of nanotubes versus the solution is estimated at 1:5. The SiC ceramic powder with sinter-activating additives (non-crystalline boron, 1% wt.) was mixed in a rotary drum mixer during 5 hours in distilled water. Further, the suspension was dried at a temperature of 70…90 °C allowing it to reach a moisture level of 3…5%; subsequently, the powder was rubbed through No 0063 sieve. The dry mix powder with additives, the polyvinyl alcohol solution and the carbon nanotubes suspension (1:5) were mixed using a planetary mill in corundum drums with corundum balls with a mass ratio of material, milling agents and medium of 1:1:2 respectively for optimal homogenization. The homogeneous suspension was dried at a temperature of 80…90 °C so that it reaches a moisture level of 5%; the powder was subsequently rubber through No 01 sieve.

The initial powder was compacted using the spark plasma sintering method in the FCT HP D5 machine. Consolidation was performed in a cylindrical graphite matrix with an internal diameter of 20 mm in a dynamic vacuum medium with a residual pressure of 3 Pa. In the course of the sintering process, the matrix was continuously compacted using a pressure of 30 MPa while heating up to 600 °C and a pressure of 50 MPa at higher temperatures. A 5-minute long degassing break took place at a temperature of 600 °C. Before sintering temperatures (1900…2000 °C) were reached, heating was carried on at a constant rate of 100 K/min. These temperatures cover the optimal temperature range of sintering of silicon carbide doped with non-crystalline boron. The exposure to the sintering temperature was 5 minutes.

Three series of samples were made with the varying content of reinforcing additives. The dry mix for the first series of samples was prepared without adding multi-wall carbon nanotubes; the second series contained 0.5 % wt. of MWCNT, the mass fraction of nanotubes in the third series of samples was 1 % wt. There was a variation in the sintering temperature within one series. Each of the series contained three samples sintered at different temperatures: 1900, 1950 and 2000 °C. The parameters of the samples of ceramics are given in Table 1. It has been found that the total porosity in the samples synthesized at a temperature of 1900 °C amounts to 18 %, at 1950 °C – 16 %, at 2000 °C – 8 %.

| Sample No | Composition | $T_{\text{sinter}}, ^\circ\text{C}$ | Picnometric density, g/cm³ |
|-----------|-------------|---------------------------------|---------------------------|
| 1         | SiC+1%B    | 1900                            | 3.11                      |
| 2         | SiC+1%B    | 1950                            | 3.07                      |
| 3         | SiC+1%B    | 2000                            | 3.01                      |
| 4         | SiC+1%B+0.5% MWCNT | 1900 | 3.10 |
| 5         | SiC+1%B+0.5% MWCNT | 1950 | 3.08 |
| 6         | SiC+1%B+0.5% MWCNT | 2000 | 3.10 |
| 7         | SiC+1%B+1% MWCNT | 1900 | 3.12 |
| 8         | SiC+1%B+1% MWCNT | 1950 | 3.09 |
| 9         | SiC+1%B+1% MWCNT | 2000 | 3.11 |
Investigation of microstructure and X-ray microanalysis of the composition were performed on samples using a scanning electronic microscope ‘FEI Versa 3D LoVac DualBeam’. Studies of elastic behavior of samples were performed using the ultrasonic spectroscopic method and the nano-indentation method. Samples for acoustic measurements were shaped as thin round-section discs with a diameter of 20 mm and a height of 2.4 mm. Young's modulus was measured in a temperature range of 20 to 1200°C. All the measurements were performed in high vacuum, which was provided by a diffusion pump. The heating rate was 12 °C/min. The temperature was measured using tungsten-rhenium thermocouples. We suggested that the value of Poisson’s ratio equals to the typical value for this type of ceramics (0.19).

Nano-indentation was performed on the cross-section of sample with 1 % wt. of CNT. We measured the elasticity modulus of grains in the structure of the composite. NanoTest 600 with a Berkovich’s diamond indentor was used. The results of measurements were not affected by the difference of samples and the indentor temperature due to preliminary holding of samples inside the chamber for 12 hours. Both before and after the indentation tests, the sample surface was scanned in order to recognize its structure, locations of pores and to establish the indentation points. The tests were performed with a force of 50 mN and 100 mN in closely located non-overlapping points. Two values of the force had to be made to verify that the material volumetric properties were measured, and not the surface properties. Value of Young’s modulus $E_s$ was calculated by a well-known approximate formula for reduced modulus $E_r$:

$$\frac{1}{E_r} = \frac{1-v_i^2}{E_i} + \frac{1-v_s^2}{E_s},$$

(1)

Here, $E_i = 800$ GPa is the indentor material elastic modulus found by the calibration on quartz samples, $v_i = 0.07$ is the diamond indentor Poisson’s ratio picked up from the table data; $v_s$ is silicon carbide grains Poisson’s ratio assumed to be amounting to 0.125.

3. Results

Micrographs of the composites structure are given in Figure 1 and Figure 2. It is clear that CNTs are positioned as large agglomerates and fill up the intergranular space and voids (Figure 2). The Micro X-ray phase analysis of the chemical composition of the samples surfaces confirmed the fact of a high volumetric content of carbon in the intergranular space area: 88% wt. as compared with 30 % wt. in the ceramics grain area (Figure 3). It was also established that in the CNT location area, there is a high oxygen concentration (4.7 % wt.) as compared with 1 % wt. in the grains area. This may indicate nanotubes oxidation in the process of cleaning or processing or in the process of powders sintering.

![Figure 1. A microstructure of SiC + CNT composite ceramics: a – an overall view, b – areas of the X-ray microanalysis.](image-url)
Figure 2. Agglomerates of CNT in the intergranular space of ceramics.

Figure 3. Results of X-ray microanalysis of samples surface: a – the results of the analysis in the area of the pore containing CNT; b – the results of the analysis in the SiC ceramics grain area.

The measurement results of Young’s modulus of nanocomposite samples reinforced by CNT at room temperature and the temperature of 1200 °C are given in Figure 4.

Figure 4. Correlation of Young’s modulus with the sintering temperature and a CNT mass fraction at room temperature (a continuous line) and at high (a dashed line) temperature.
An estimated measurement error is ±3%. It was found that the increase in the sintering temperature of ceramic composites results in an increase of the Young's modulus. The maximum value of the modulus takes place for the composite sintered at a maximum temperature in the absence of nanotubes. Such behavior of Young’s modulus may be explained by the impact of residual porosity at lower sintering temperatures and by the degradation effect due to CNT agglomerates.

The nano-indentation results are given in Figure 5 and Table 2. Figure 4b shows the indents on the sample surface after experiments. The dependence of indentor penetration depths on the applied force was revealed. Based on these data the NanoTest 600 system software enabled automatic estimation of a reduced elastic modulus value and a hardness value in the indentation point (Table 4). The resultant average value of the ceramics grains reduced elastic modulus amounted to 344 GPa. The spread of values for six points reached 10...14%. The grains Young’s modulus found by formula (1) amounted to 591 GPa.

![Figure 5](image_url)

Figure 5. The ceramics cross section surface structure scanned with NanoTest 600: a – indentation points; b – indents on the sample surface.

| Indent No | Maximum Depth, nm | Force, mN | Depth Of Trace, nm | Hardness, GPa | Reduced Modulus, GPa |
|-----------|-------------------|-----------|--------------------|---------------|---------------------|
| 1         | 322.2             | 50        | 248.4              | 29.9          | 336.9               |
| 2         | 361.3             | 50        | 290.2              | 22.3          | 301.9               |
| 3         | 341.4             | 50        | 268.0              | 25.9          | 315.4               |
| 3         | 442.6             | 100       | 340.0              | 33.1          | 360.3               |
| 4         | 401.9             | 100       | 308.1              | 39.9          | 432.7               |
| 5         | 469.5             | 100       | 359.1              | 29.8          | 317.9               |
| **Mean**  |                   |           |                    | **30.2**      | **344**             |
| Mean deviation: |               |           |                    | 4.2 (14%)     | 34 (10%)             |

### 4. Conclusions

The study of SiC-CNT nanocomposite ceramics samples by means of spark plasma sintering has been conducted. It has been established that carbon nanotubes in the structure of sintered composites are located as agglomerates in the intergranular space of ceramics. An addition of CNT causes the composite ceramics elastic modulus to decrease. As it has been revealed from nanoindentation measurements, the silicon carbide grains stiffness characteristics turn out to be equal, approximately, to the theoretical value of ideal SiC crystals stiffness. It has been found that the best option of the
ceramics sintering modes is exposure to 2000 °C. In this case, composites have the smallest volumetric fraction of porosity and the highest values of elastic modulus. The addition of CNT causes the ceramics Young’s modulus to reduce. Therefore, the nanotubes may act as defects in the structure of composite and intergranular phase stiffness characteristics decrease due to the presence of multi-walled CNT agglomerates.

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