Preparation and properties of a composite SiC with addition of multi-walled carbon nanotubes synthesized in the plasma jet

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Abstract. Ceramic composite reinforced with plaits of carbon nanotubes have been fabricated by the reaction bonded silicon carbide method. Carbon nanotubes (CNTs) are produced using a 35 kW dc plasma torch and C₂H₂ as carbon precursor. Effective methods of CNTs adding and dispersing in the preform volume have been found. The optimal content and operational technological parameters have been determined for ceramic matrix. Physico-mechanical properties of the reinforcing ceramic matrices with nanomaterials have been investigated.

1. Introduction

Silicon carbide based advanced ceramics are the leading materials for a number of applications in aeronautics, energy, electronics, nuclear, and transportation industries [1]. Specifically SiC based materials are able to preserve durable working capability when exposed to radiation at high temperatures and in aggressive environments. Silicon carbide ceramics have high stiffness and excellent thermal stability with low density, but their brittleness impedes their use as structural materials. Because of their exceptional resilience, carbon nanotubes (CNTs) might be desirable as reinforcement for ceramics [2]. The combination of these nanotubes with a ceramic matrix could potentially create composites that have high temperature stability as well as exceptional toughness and creep resistance. According to the data [3], the addition of 0.25 wt % CNTs to ceramics based on silicon carbide leads to an increase in strength by over 30%.

Reinforcing ceramic matrices with nanomaterials continue to hold promise but with significant challenges to real success. Given the costs of the materials and processes involved, it is not sufficient to obtain marginal improvements in properties over traditional micron-scale composites or virgin matrices. The point is what exact method of CNTs synthesis will provide for production of nanotubes with controlled morphology and in big quantities which will reduce their cost and the cost of a nanocomposite.

Considerable increase of the synthesis productivity rate and time may be achieved due to the transfer to synthesis into a volume, in particular, at use of a plasma torch. Prospects for the directions of research in plasma torch application are confirmed by the results of the study [4], where an induction type serial plasma torch was used in a plasma jet reactor. The presented
data on CNTs synthesis productivity rate show that it is much higher than the productivity achieved using the electrical discharge and laser synthesis methods. Whereas the CNTs quality is not behind their quality at electric-arc jet or in the use of lasers.

The addition of a second reinforcing phase in ceramics has been an effective practice to improve their toughness, converting brittle ceramics into practical engineering materials. To use chosen nanomaterials as the reinforcement to form advanced composites, it is crucial to achieve a good CNTs dispersion within the matrix.

Many efforts have been put in to modify the surface properties of carbon nanotubes. A simple mechano-chemical functionalization of the CNT surface [5] or application of different coatings [6] may be prospective choices to enhance nanotube–matrix bonding. The manufacture of a ceramic composite generally requires high temperatures. Therefore, the high temperature degradation process of CNTs has to be further clarified to achieve a proper protection of CNTs at high temperature processes. This study is focusing on the preparation processes that allow to tailor the microstructure of carbon nanotube reinforced silicon carbide-based ceramic composites. Experimental procedure has been conducted to effectively disperse in the matrix the CNTs synthesized in the plasma jet. Morphological, structural observations, as well as characterization of mechanical and thermophysical properties will be presented.

2. Methods
For production of a ceramic material based on nanocomposite silicon carbide/carbon nanotubes, the technology of reaction bonded silicon carbide was used in the study. Reaction bonded silicon carbide (RBSC) composites are two-phase materials consisting of silicon carbide (SiC) and silicon (Si). Reaction bonded SiC ceramics are the subject of particular due to large size and complex shape capability. In the use of this technology the volume of required mechanical processing for the final product is minimized which serves as an additional cost reducing factor.

RBSC is made by infiltrating compacts made of mixtures of SiC and carbon with liquid silicon. The silicon reacts with the carbon forming silicon carbide. The reaction product bonds the silicon carbide particles. Any excess of silicon fills the remaining pores in the body and produces a dense SiC–Si composite.

In practice, the carbon content in the SiC and the particle size distribution are changed within wide limits. The resulting products are made with a wide range of compositions and properties. At one extreme, carbon fiber felt or cloth can be infiltrated with liquid silicon, whilst at the other extreme, an impervious silicon carbide body can be made with a small amount of carbon.

Most reaction bonded silicon carbide is made with formulations that contain an organic plasticizer, carbon and silicon carbide particles. This mixture is ideally suited to near net formation by pressing, injection molding or extruding. Further, since the reaction process typically gives a dimensional change of < 1%, manufacturers have excellent control of component tolerances.

In the study a plasma jet reactor was used for CNTs synthesis. A detailed description of the experimental setup was given in the study [7]. The reactor includes a vacuum chamber filled with inert gas, graphite cylinder, movable metal collector and a target which are installed perpendicularly to a plasma flow, a plasma torch with coaxially placed electrodes. The most important part of the reactor is a plasma torch with the vortex stabilization of working gas and expanding channel of output electrode. Output electrode nozzle profiling and internal electrode front face positioning in the nozzle neck ensure regular dynamic pressure, parameters consistency and arc stabilization along the entire length of its positive column, device operation stability and better heat exchange in the arc initial path.

The essence of plasma jet nanomaterials synthesis in contrast to a widely used arc method is that the carbon containing materials together with a working gas (argon, helium) are supplied to a direct current plasma torch with expanding channel-anode after which they evaporate in
Table 1. Technological conditions.

| Power (kW) | Current (A) | Voltage (V) | Gas | Helium flow rate (Torr) | Argon flow rate (g/sec) | Acetylene flow rate (g/sec) |
|------------|-------------|-------------|-----|-------------------------|-------------------------|-----------------------------|
| 30–40      | 350–400     | 60–110      | 50–750 | 0.5–0.9                | 3.0–3.75               | 0.05–0.16                   |

a plasma jet with further shock chilling of generated carbonic vapor with formation of carbon nanotubes in the gas volume as well as on the surface of solid materials. For each experiment hydrocarbon was added after temperature field setup in the graphite reactor. As a rule, it amounted to 5 minutes and was defined by water temperature in the cooling channels. Helium and argon were used as a working plasma-forming gas. The experiments were carried out at plasma torch electric power output in the range 24–40 kW. Plasma torch current value was maintained in all series at a constant level of 350–400 A. Anode-cathode path was 2 mm. The arc voltage was changed from 70 to 105 V, depending on the experimental conditions (type of plasma-forming gas and its flow rate). Helium was used for pressures 200–710 Torr and at flow rate variation from 0.75 to 1 g/sec, argon flow rate was from 3.5 to 3.75 g/sec and under 150–730 Torr pressures. Duration of the experiments was 10–20 minutes. In the experiments acetylene was used as a source of carbon. Gas phases proportion (acetylene and plasma forming gas) in the mixture was varied by the flow rates. The experimental conditions are presented in table 1.

Method of electron microscopy was used to investigate the structure of the synthesized products on a scanning electron microscope of MIRA 3 TESCAN with Schottky field emission cathode in high vacuum regime. Raman spectra were investigated by using the exciting radiation at a wavelength of 532 nm (Ntegra spectrum). X-ray diffraction data were obtained at room temperature on a powder diffractometer Stoe Stadi P.

Efficiency of the synthesis, thermal stability and phase composition of carbon products were evaluated by thermogravimetry and differential scanning calorimetry on a synchronous thermal analyzer STA 409PC Luxx (NETZSCH) with linear heating sample in air at the rate of 10 K/min at temperatures up to 1000°C.

The measurements of apparent density, open porosity and water absorption of the ceramic samples were performed by the method of hydrostatic weighing. Fracture strength under room temperature was defined at 3-point bend. Stress intensity factor (stress factor) and Vickers microhardness for the basic phase were measured by the method of indentation with 300 g load on DuraScan 50. X-ray phase analysis of SiC/CNTs nanocomposite matrix was conducted on facility DRON-6 with the use of program complex PD Win (radiation Cu $K_\alpha$, filter Ni) according to method PM 596.1541-2002.

3. Results of the experiments

The experiments on acetylene decomposition in a plasma jet reactor have shown that the highest yield of CNTs is achieved at use of helium as a plasma forming gas at 350 Torr pressure. Whereas the amount of nanostructured carbon amounts to 75% (figure 1). Thermogravimetric analysis has shown the shift of CNTs oxidation temperature interval toward the higher temperatures area. It relates to that the forming structures are gathered in clusters. Figure 2 presents microphoto of the synthesis products. It is seen that the CNTs have a shape of plaits, i.e. laced nanostructures.

Using the RBSC technology there was prepared an initial batch mixture of two types in which, without preliminary purification, CNTs were added in amount of 0.01; 0.05; 0.1; 0.5 and 1.0 wt % (table 2). The amount was defined by the mixture color change from gray to black.
Figure 1. Results of thermogravimetric analyses of products of synthesis by decomposition of acetylene at a pressure of 350 Torr; plasma forming gas is helium: (1) loss of weight; (2) heat flow; (3) rate of generation CO$_2$.

Figure 2. Morphology of synthesis products from the decomposition of acetylene at a pressure of 350 Torr. Helium flow rate is 0.75 g/sec and acetylene flow rate is 0.11 g/sec.

For dispersion of CNTs throughout the volume, for the reason of their high hydrophobia, a special additive was introduced in the ceramics composition—a disperser based on sodium salt of poly carbonic acids. Its type and quantity were determined through experiments. The optimal amount of DOLAPIX was 2 wt %. Coating CNTs by the dispersive substance turned to be an effective method to change CNTs hydrophobic nature to hydrophilic and increase CNTs dispersive ability in solution with isopropyl. Modified CNTs were homogenously blended with SiC on a micro-level due to heterocoagulation. Such blending method increased the chemical compatibility between CNTs and SiC which is important for the enhancement of boundary strength between them. Powders of green silicon carbide of grade mark 64C grit F500 and F1200 were used (table 2).
Table 2. Initial composition of the batch mixture.

| Composition N | Quantity content of the batch mixture components, % mass | SiC F500 | SiC F1200 | CNTs |
|---------------|----------------------------------------------------------|----------|-----------|------|
| 1             |                                                          | 60       | 40        | —    |
| 2             |                                                          | 60       | 39        | 1    |
| 3             |                                                          | 60       | 39.5      | 0.5  |
| 4             |                                                          | 60       | 39.9      | 0.1  |
| 5             |                                                          | 60       | 39.95     | 0.05 |
| 6             |                                                          | 60       | 39.99     | 0.01 |

Table 3. Properties of materials.

| Properties                     | 1   | 2   | 3   | 4   | 5   | 6   |
|--------------------------------|-----|-----|-----|-----|-----|-----|
| Density, g/m³                  | 2.86| 2.87| 2.86| 2.86| 2.86| 2.86|
| Open porosity, %               | 0.2–0.3| 0.1–0.4| 0.1–0.4| 0.2–0.6| 0.1–0.4| 0.1–0.4|
| Bending strength, MPa          | 290±10| 335±10| 345±10| 330±10| 300±10| 300±10|
| Stress factor, MPa m¹/²        | 2.5–3.4| 2.5–3.4| 3.5–4.3| 3.0–4.0| 3.0–3.4| 2.5–3.4|
| Microhardness, GPa             | 19–23| 19–23| 19–23| 19–23| 19–23| 19–23|

Regimes of CNTs dispersion in SiC based powder materials were practiced in a planetary mill. It was established that the optimal time of blending in isopropyl alcohol solution was 12 hours at 150 rotations per minute. The samples sized 70 × 70 × 10 mm³ were produced by the method of semi-dry compressing in steel press-molds on a press brand P-250 under 75 MPa pressure which allowed to produce semi-finished product with the highest compaction degree. Subsequently the samples were subjected to pyrolysis in a nitrogen media and silicification by silicon vapors in vacuum under temperature 1850 °C in a high-temperature vacuum furnace VHT 40/22-GR. After silicification, the samples were subjected to treatment at abrasive-jet tool to remove silicon sags from their surface.

The final samples were examined to define the mass, apparent density, microstructure and phase composition and for evaluation of the physical-chemical properties. Table 3 presents the properties of the materials. One of the major characteristics of the ceramic materials is strength limit in bend.

For all compositions the apparent density values are on the same level ∼ 2.86 g/cm³. The highest values of strength limit in static bend (σbend) under room temperature 345 MPa are observed for the samples with CNTs addition in amount of 0.5% mass. No substantial differences are noticeable in the major phase micro hardness in all compositions. All values are in the range 19–23 GPa. Maximal value of the stress intensity factor also corresponds to the composition with CNTs addition in amount 0.5 wt %. Investigation of CNTs distribution regularity in the semi-finished samples was conducted with scanning electronic microscope EVO 40 XVP and x-ray micro analysis system Quantax 400 (PCMA). X-ray phase analysis in all samples has shown the presence of the major crystal phase—α-SiC (hexagonal, poly type 6H), β-SiC (cubical, poly type 3C) and big amount of free silicon Si (cubical).

Figure 3 presents the microstructures: a–semi-finished sample 1 and b–sample 2 with addition of 1% CNTs. Microstructure of sample 1 is presented by clearly drawn big grains of milled shape with size up to 20 μm and small grains of indefinite shape up to 5 μm, regularly distributed.
between the big grains. Microstructure of sample 2 with 1 wt % CNTs (figure 3b) contains 3rd phase of amorphous shape, regularly distributed across the entire sample surface and forming agglomerations in some places. When magnified ten thousand times clusters of laced ropes become visible in the microstructure. Figure 3b presents such results.

Complete x-ray spectral analysis of the sample has confirmed the presence of elementary carbon in the amorphous phase. Figure 4 presents the cartogram of the sample surface elements and their distribution character.

Thus, within the study framework the research was conducted to produce and investigate the properties of the samples of RBSC modified by CNTs in amount of 0.01%, 0.05%, 0.1%, 0.5%, 1.0%. The samples were silicificated in the standard regime for the initial material. For all compositions the values of apparent density are on the same level \( \sim 2.86 \text{ g/cm}^3 \). With the increase of CNTs additive content from 0.01 to 0.5% the growth of strength limit in static bend is observed from 290 to 345 MPa and creep resistance from 2.5 to 3.5 MPa m\(^{1/2}\). At further increase of the additive the \( \sigma_{\text{bend}} \) and a stress intensity factor values drop. The maximal achieved fracture toughness (4.3 MPa m\(^{1/2}\)) is higher than the value of 3.7 MPa m\(^{1/2}\) for single-edge-precracked-beam method \[8\]. Examination of the semi-finished samples has shown that mixing in planetary mill during 12 hours allow to regularly distribute the nanotubes clusters...
along the material structure, but we have failed to break the clusters into separate nanotubes, in the result the separate conglomerations of the clusters are seen between the grains of silicon carbide.

4. Conclusion
Experimental samples of nanocomposite silicon carbide /CNTs were produced with enhanced physico-mechanical properties: density from 2.857 to 2.881 g/cm$^3$, open porosity 0.27–0.43%, water absorption 0.05–0.1%. According to the electronic microscopy data on the modified ceramic chipping containing 1 wt % of CNTs, unwinding and straightening of nanotubes does not occur which is the key moment in the possibility to receive a composite, possessing both features–high creep resistance and high strength, which is a non-typical combination for ceramic materials. On the basis of the experimental results the mutual relation has been established between physical-mechanical properties of the silicon carbide based ceramic materials and the material phase composition. The silicon carbide-based advanced ceramic nanocomposites produced by this process are denser, have tailorable microstructure and mechanical properties, and can incorporate second phases without the detrimental effects of unwanted sintering aids. Improvement of the nanocomposite creep resistance provide for CNTs cluster shape which hydrophobic nature may easily change to hydrophilic due to the use of a dispersion additive. The optimal regimes of plasma jet method for CNTs production in large scale have been found.

Acknowledgments
The authors gratefully acknowledge the Russian Foundation for Basic Research for the support by grants No. 15-08-00165 and 16-08-00145.

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