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Mathematical Modeling of Spark Plasma Sintering of Silicon Carbide Composite Modified with Carbon Nanotubes

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An experimental study of the process of obtaining a ceramic composite material based on SiC reinforced with carbon nanotubes (CNTs) with content of CNTs of 1-3 % by the method of spark plasma sintering is carried out. A mathematical model of the porosity variation during the sintering process has been developed. On the basis of experimental studies and mathematical modeling, an optimal sintering regime has been found. A flow chart for the preparation of a SiC-CNT ceramic composite with a content of 1 - 3 % CNT in a laboratory scale in the software package Honeywell UniSim Design (v.3.9) is presented.

1. Introduction

Composite materials are superior to traditional materials by their properties, having a lower density. To expand the range of properties of composite materials, several matrices or several kinds of fillers are used. Composites with a ceramic matrix are used as heat-resistant and wear-resistant materials, which is due to its high hardness, modulus of elasticity, low density and high melting point.

Ceramics based on silicon carbide is used to create nuclear reactors, high-pressure jet nozzles and the creation of corrosion and erosion-resistant high-temperature materials (Zhitnyuk, 2014). There are areas of application of ceramics, for which the increase in fracture toughness and hardness is especially important, since they are associated with large shock loads. Such areas include the manufacture of ceramic cutting tools, coatings for high-temperature engines and armor-ceramic plates. Possessing high thermal, chemical, radiation resistance and mechanical strength, oxidation resistance among many alloys and chemical compounds, well resists erosion, corrosion, wear - silicon carbide is considered to be the most promising material for the manufacture of a ceramic matrix based on it. The friability of silicon carbide is a consequence of the crystal structure and the type of chemical bond and is combined in it with high hardness (Kapustin et al., 2015).

The main task solved through the formation of composite structures based on it is to make the final material highly crack resistant. To increase and stabilize the mechanical properties of composites based on silicon carbide, such as strength, fracture toughness and elastic modulus, apply methods of reinforcing ceramic composites using nanotubes. An important feature of carbon nanotubes (CNTs) is their ratio of length to diameter, it affects the transfer of the load from the matrix and the effectiveness of strengthening. They belong to the most rigid and strong fibers, with Young modules reaching 1 TPa, and a tensile strength of up to 63 GPa (Duong et al., 2015). The stability of the carbon fiber to the faults is much higher than that of a pure ceramic matrix. Thus, the combination of a carbide matrix with carbon nanotubes can increase the strength characteristics of the SiC-CNT composite. Since the synthesis of ceramics based on silicon carbide is carried out at temperatures> 2,000 °C, there is a need to create a new composite material that will preserve the properties of ceramics and reduce the sintering temperature. For this purpose, an alumina-magnesia spinel is added to the matrix based on silicon carbide, to obtain a composite material with the composition $MgAl_2O_4$ – 45 % by weight. SiC is 55 % by weight.

The combined use of powders of oxide and anoxic compounds makes it possible to increase the oxidative stability of the composite material by blocking the particles of the oxygen-free compounds from oxidation.

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Sintering of covalent silicon carbide, which is one of the most promising oxygen-free refractory compounds for the production of high-temperature structural materials, is carried out at high temperatures (1,800 - 2,200 °C) with a small amount of additives and / or using high pressures. When hot pressing of silicon carbide powders without additives, products with high porosity are obtained. Using the technology of spark plasma sintering can reduce the maximum temperature and reduce the total compaction time of powder compacts and reduce the final porosity of the material. At low atmospheric pressure, under the action of a pulsed electric current, spark plasma regions appear in the material, having a high temperature (up to 10,000 °C) (Fedosova, 2016). Such high local temperatures make it possible to achieve high rates of removal of intercrystalline porosity.

2. Experimental research

The objective of the experiment was to synthesize a composite material based on SiC and carbon nanotubes (1-3 % by weight). In the production of a composite material, an industrial silicon carbide powder (grade F1200) was used with an average grain size of 2.5 μm. Powders of $MgCO_3$ and α-$Al(OH)_3$ were used to prepare an alumina-magnesian spinel ($MgAl_2O_4$), which is used as an auxiliary additive in the ceramic matrix of silicon carbide. Dispersing ultrasound of CNTs (multilayered carbon nanotubes obtained by gas-phase pyrolysis of a methane-hydrogen mixture) was carried out in an aqueous solution of polyvinyl alcohol (1 %). Uniform distribution of CNTs in the volume of the silicon carbide and spinel matrix and obtaining homogeneous mixtures, followed by stirring of the dispersed suspension. Rotation and polishing for 40 min at a speed of 600 r/s. The resulting mixture was dried at a temperature of 70 °C. Granulation of the powder was achieved by grinding through a sieve with a mesh size of 100 and 200 μm. The sintering of the composite with the SiC-$MgAl_2O_4$-CNT composition (1 - 3 % by weight of CNT) was carried out by the method of spark plasma sintering at a pressure of 15 kN, heating to 1,550 °C for 3 min, then heating to 1,700 °C for 3 min, and holding 5 and 10 min. The temperature regime parameters for the samples of spark plasma sintering are presented in Table 1.

Table 1: Temperature conditions of spark plasma sintering of samples of the SiC-CNT composite

Number of the mode	CNT content, % wt.	Heating temperature, °C	Holding temperature, °C	Heating time up to 1,550 °C, min	Heating time up to 1,700 °C, min	Holding time, min
1	1	1500	1700	3	3	5
2	1	1500	1700	3	3	10
3	2	1500	1700	3	3	5
4	2	1500	1700	3	3	10
5	3	1500	1700	3	3	5
6	3	1500	1700	3	3	10

Table 2 presents the results of calculations of water absorption, porosity, density, strength and microhardness of the samples on the basis of the results of experimental studies of samples of the SiC-CNT composite.

Table 2: The results of calculations of the properties of samples of a SiC-CNT composite

Number of the mode	Water absorption, %	Porosity, %	Density, g/cm^3	Flexural strength, MPa	Average microhardness, GPa
1	3.8	15.3	3.18	223	16.8
2	3.0	12.4	3.09	347	20.9
3	4.9	19.5	2.66	232	11.6
4	5.4	17.2	2.69	358	25.3
5	3.4	19.5	3.12	218	13.1
6	5.1	16.4	2.86	356	24.4

As a result, a composite was obtained with a crystal-equal structure and a uniform distribution of nanotubes in the matrix, demonstrating bending strength up to 358 MPa and porosity < 20 % at a sintering temperature of 1,700 °C.

3. Mathematical modelling

Based on the results of studies of the properties of samples of a ceramic composite SiC-CNT, it can be noted that the final porosity depends on the amount of CNTs and the holding time.

Mathematical modeling of the description of the process of spark plasma sintering was carried out for the regimes presented in Table 1.

When composing a mathematical description, changes in the porosity of the composite during the spark plasma sintering are taken into account as the following parameters: heating rate at each stage, current temperature, intermediate heating temperature, maximum heating temperature, pore size, heating time of each stage, holding time, CNT content in the composite.

The main characteristic for constructing a mathematical model is the porosity of the material, since it affects the physic-mechanical properties of composites. These properties are taken into account when compiling a mathematical description of the porosity of the composite during the spark plasma sintering as the following parameters: the heating rate at each stage, the intermediate heating temperature, the maximum heating temperature, the heating time of each stage, the holding time, the CNT content of the composite, the current state of the powder pressing.

The pore size distribution function *f (t, l)* describes the process of porosity reduction during sintering. This function reflects the state of the powder compact at time *t*. The equation describing the process of decreasing pores (Fedosova et al., 2016) has the form:

$$\frac{\partial f}{\partial t} - \frac{\partial f\,\eta(t,l)}{\partial l} = 0; \quad t \in [0;t; \quad l \in [0;L], \tag{1}$$

f (t, l) - function of the pore size distribution, *t* - process time, *η* - rate pore penetration, and *l* - pore diameter.

For the first sintering stage (heating stage), the driving force of the process *(l)*, the heating rate *(ΔT / Δt)*, the current temperature *(T)*, the volume fraction of the CNT (V_{CNT}). For the second and third stages, the difference between the sintering temperatures T_{max} and the shrinkage rate temperature $T_{\Delta l}$. The following relations are introduced:

$$\eta_1 = k_1\left(\frac{\Delta T}{\Delta t}\right)^{m_1} \tag{2}$$

$$\begin{cases} k_1 = a_1 + b_1\sqrt{l^3} + c_1 T \\ a_1 = a_{10} + b_{10}V_{\text{CNT}} + c_{10}V_{\text{CNT}}^2 \end{cases} \tag{3}$$

$$\eta_2 = k_2\left(T_{\text{текущая}} - T_{\Delta l}\right)^{m_2} \tag{4}$$

$$\begin{cases} k_2 = a_2 + b_2\sqrt{l^3} \\ a_2 = a_{20} + b_{20}V_{\text{CNT}} + c_{20}V_{\text{CNT}}^2 \end{cases} \tag{5}$$

$$\eta_3 = k_3\left(T_{\max} - T_{\Delta l}\right)^{m_3} \tag{6}$$

$$\begin{cases} k_3 = a_3 + b_3\sqrt{l^3} \\ a_3 = a_{30} + b_{30}V_{\text{CNT}} + c_{30}V_{\text{CNT}}^2 \end{cases} \tag{7}$$

η_1, η_2 and η_3 – the rate of decrease pore size on the 1st, 2nd and 3rd stages of sintering; k_1, k_2 and k_3 - phenomenological coefficients considering dependence of the speed of pore size decrease from the CNTs volume V_{CNT} (parameters a_1, a_2 and a_3); the current size of the pores *l* and the current temperature in the sintering chamber *T*; m_1, m_2 and m_3 – constants characterizing the degree of deviation of system from balance state for the 1st, 2nd and 3rd stages of sintering.

To solve Eq(1), we used an absolutely stable scheme of difference approximation - "Z-scheme" (the scheme has a second order of approximation in time t and coordinate). The difference scheme looks like:

$$\frac{f_j^{n+1}-f_j^n}{\Delta t}-\frac{1}{2}\left(\frac{f_{j+1}^{n+1}\eta_{j+1}^{n+1}-f_j^{n+1}\eta_j^{n+1}}{\Delta l}+\frac{f_j^n\eta_j^n-f_{j-1}^n\eta_{j-1}^n}{\Delta l}\right)=0 \quad (8)$$

Δt – time step, Δl – a space step (pore size), index n is responsible for the time step, index j - per space step. The difference scheme Eq(8) is implicit and, because of its absolute stability, the value of the ratio $\Delta t / \Delta l$ does not affect its solution.

The calculated value of the porosity was calculated according to the formulas:

$$V_{\text{пор}}=\int_0^{L_{\max}}\frac{4\pi}{3}\left(\frac{l}{2}\right)^3 f(l)\,\mathrm{d}l \quad (9)$$

$$\varepsilon=\frac{V_{\text{пор}}}{V_{\text{пор}}+V_{\text{тв}}}100\% \quad (10)$$

$V_{пор}$ – total pore volume, $V_{тв}$ – total solid volume, ε – porosity of the composite.

The resulting mathematical model of spark plasma sintering describes changes in the porosity of a powder compact during its consolidation. The kinetic constants (Table 3) that enter into the mathematical model take into account the influence of the physical parameters of the various stages of sintering. Search for constants was carried out by scanning from the condition of equality of calculated and experimental data.

Table 3: Values of the kinetic constants of the process of spark plasma sintering of a composite powder

The first stage of sintering (heating)		The second stage of sintering (heating)		The third stage of sintering (delay)	
constant	value	constant	value	constant	Value
a_{10}	$1.4*10^{-3}$	a_{20}	$1.3*10^{-2}$	a_{30}	$0.6*10^{-2}$
b_{10}	$-1*10^{-3}$	b_{20}	$-2*10^{-2}$	b_{30}	$-3*10^{-2}$
c_{10}	$4*10^{-3}$	c_{20}	$9*10^{-2}$	c_{30}	$9*10^{-2}$
b_1	$2.7*10^{-3}$	b_2	$2.7*10^{-2}$	b_3	$4.6*10^{-2}$
c_1	$2.3*10^{-3}$	c_2	$4*10^{-2}$	n_3	0.5
n_1	1.8	n_2	1.8		

In heating stages (1 and 2 stages of sintering), the driving force of the process of decreasing porosity is the rate of heating. The degree of the system deviation from the equilibrium state is set using the kinetic constants that characterize the effect of the concentration of the reinforcing filler in the composite powder, the heating rate, the current temperature, and current size of the pores. For the first stage, the dependence of the rate of change in the pore size on the number of CNTs in the volume of the composite, the current pore size, and the current temperature of the furnace chamber was taken into account. For the second step of heating the driving force reduction process a porous powder compact composite SiC-CNT is the rate of heating, the difference between the temperature of the second stage and the temperature change composite shrinkage rate.

For the stage of temperature aging (stage 3 of sintering), the driving force of the process is the difference between the soaking temperature and the temperature of the shrinkage rate change of the SiC-CNT composite. Taking into account the kinetic constants, the influence of the amount of reinforcing filler, the soaking temperature, the shrinkage rate change temperature, the current pore size takes into account. It is established that for the temperature-holding stage the rate of decrease in the pore size depends on the amount of CNTs in the volume of the composite and on the current pore size.

The presented mathematical model describes the behaviour of the porous space of the composite powder, taking into account all the features of the spark plasma sintering process and reflects the initial state of the powder compacting through the initial and boundary conditions. The initial conditions of the mathematical model take into account the pore size distribution determined by the law of normal distribution so that the initial porosity is equal to the calculated initial porosity. The resulting mathematical model Eq(2) - Eq(7) used for numerical experiments in order to identify optimal temperature, and to determine the change in pore size distribution function, changes in the average pore diameter and overall porosity of the powder compacts at each time point. The optimum regime of spark plasma sintering of a SiC-CNT composite with a porosity of <15% can be obtained with a CNT content of 1.5 % by weight (Figure 1) at a temperature mode: a heating rate of 366 °C/min in the

first stage, an intermediate temperature of 1,550 °C, a maximum temperature of 1,700 °C. Figure 1 and Figure 2 show results of numerical experiment for composite SiC-CNT (1-3 %vol.) which was sintered with maximum temperature 1,700 °C.

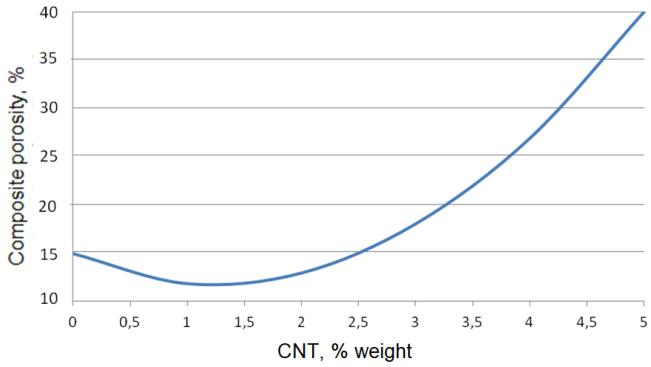

Figure 1: Results of calculations of porosity change of composite powder.

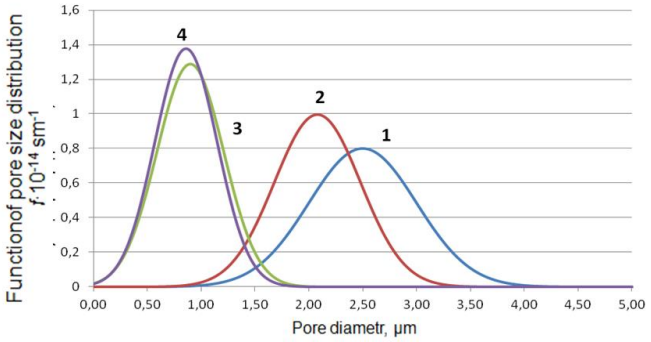

Figure 2: The nature of the change in the shape of the pore size distribution function when calculating the porosity variation of the composite SiC-CNT powder (1% CNT) in the process of spark plasma sintering (Mode No. 1): 1 - before sintering, 2 - after the 1st stage, 3 - after 2 stage 4, after the third stage of sintering.

4. Development of technological scheme

The software package Honeywell UniSim Design (v.3.9) (Koltsova et al., 2016) was used to construct a flow chart for the production of ceramic composite SiC-CNT in laboratory condition.

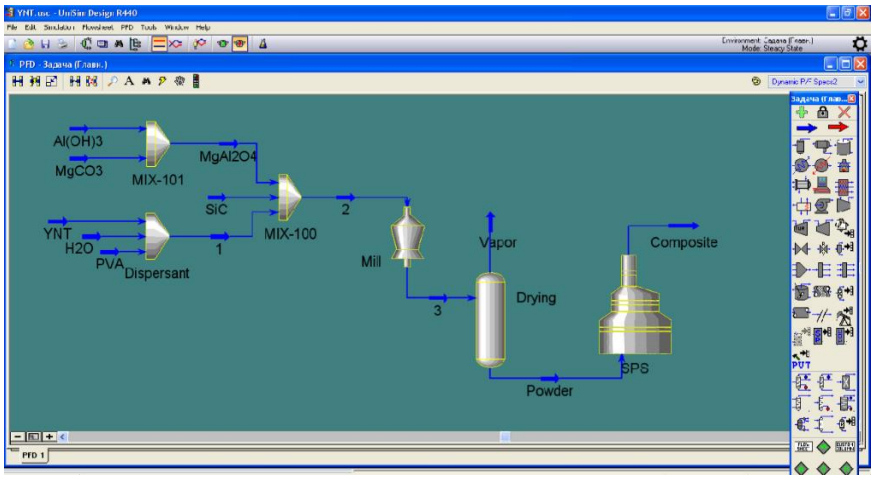

Figure 3: Technological scheme of production of ceramic-composite SiC-CNT composite, designed in the software package Unisim Design.

The selected devices were placed in the working environment of the software package and connected together in the order of production stages (Figure 3). Flows of the process flow components were then created: $Al(OH)_3$, $MgCO_3$, SiC (silicon carbide flux), YNT (flow of carbon nanotubes), PVA (flow of polyvinyl alcohol), H_2O (water flow). To account for the properties of the components, an integrated package of properties of substances used as components was connected. Included in the scope of supply: input streams of components, components compliance, temperature and pressure in the device. The PVA, YNT and H_2O streams enter the dispersant, a mixture of the inlet streams (stream 1) is added at the outlet of the dispersant. The flows of $Al(OH)_3$ and $MgCO_3$ are mixed, forming a stream of $MgAl_2O_4$. Then, stream 1, the $MgAl_2O_4$ stream and the SiC stream are fed to the inlet to the homogenizer, where the liquid and main components are mixed. After homogenization, the resulting suspension (stream 2) is ground in a mill and the stream 3 is recycled. At the output we get a composite powder (stream 3), which is fed to the dryer, where the water evaporates and leaves with the flow. Vapor, and the residual mixture (powder flow) is fed into the sintering furnace. In the flow Composite set finished composite after sintering.

5. Conclusions

A mathematical simulation of the process of obtaining nanocomposites based on silicon carbide using carbon nanotubes as a reinforcing component was performed. The values of the kinetic constants of the mathematical model are determined. A mathematical model of the description of the process of spark plasma sintering of the ceramic-composite SiC-CNT composite (1-3 % by weight) is presented on the basis of the application of the equation of the pore number-size balance (the first-order partial differential equation), taking into account the physic-chemical essence of all the phenomena occurring on stages of heating and soaking. Dependences of the variation in the porosity of the composite and the average pore size over time in the process of spark flame sintering are established. The optimal mode for obtaining a composite SiC-CNT (1-3 % by weight) with a porosity of < 15 % can be obtained by the method of claim plasma sintering with a heating rate of 366 °C / min in the first stage, an intermediate temperature of 1,550 °C and a maximum temperature of 1,700 °C at an exposure time of 10 min with a CNT content of 1.5 % by weight. In the software package Honeywell Unisim Design, a process flow diagram was constructed that includes apparatus for producing composite material corresponding to all parameters necessary for the process of obtaining a composite on a laboratory scale. This scheme can be used as a basis for scaling in the construction of the production line of the composite SiC-CNT.

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