Research Article

Structural Evolution of Silicon Carbide Nanopowders during the Sintering Process

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Processes of sintering of silicon carbide nanopowder were investigated. Values of density ($\rho = 3.17 \text{ g/cm}^3$) and strength ($\sigma = 450 \text{ MPa}$) were obtained. Within the theory of dispersed systems, the temperature evolution of the materials structure was considered. The relationship between sintering temperature, characteristics of crystal structure and physical properties, in particular, density, and strength of aforementioned ceramics was established. It was concluded that it is necessary to suppress the anomalous diffusion at temperatures above 2080°C .

1. Introduction

High-density silicon carbide ceramics have a set of unique physical and mechanical properties such as high thermal conductivity, strength and wear resistance, corrosion resistance, resistance to high thermal and mechanical stresses, thermal conductivity, and semiconductor type of conductivity [1–3]. Products from SiC can operate in chemically corrosive environments at high mechanical and thermal loads. They are promising for applications in mechanical engineering, shipbuilding, metallurgy, gas and oil industry, and energetics (sealing rings for high-loaded friction units, heat-conducting substrate). Recently, a steady trend of expansion of field of use of SiC-materials in electronics, heat-conducting substrate, and semiconductor functional heterojunctions was outlined [4]. Sufficient frequent application SiC-ceramics are found in defense industry (armor ground of combat technical equipment, turbine blades for missiles, etc.) [5].

For a long time, obtaining products with complex shapes from SiC was hampered by extremely difficult conditions of sintering of micron powders. Using of hot-pressed methods (at pressures up to 1000 MPa) at operating temperatures of about 2100°C with subsequent polishing of products using diamond tools was required. Low technology and high cost

of products manufacturing from SiC limited the applicability of this material in engineering.

With the advent of powder nanotechnologies [6], a unique opportunity of sintering of high-density silicon carbide ceramics within the traditional ceramic technology appeared. Prospects for improving in multiple time manufacturability and for reducing a cost of products are opened.

In particular, the possibility of sintering of products with complex shapes (geometric) and fine details, such as heat-removing substrate, offers the prospects of significant reduction in price of element base of electronics and solar energetic [7–9].

However, the process of sintering of SiC nanopowders within the ceramic technology currently is not fully understood.

The aim of this work was to study processes of structure formation during sintering of SiC nanopowder under laboratory conditions for establishment of relationship: temperature conditions of sintering—structure—physical properties.

2. Experimental

As starting material, a nanosized ($d = 30 \text{ nm}$) silicon carbide powder $\alpha\text{-SiC}$ with addition up to 2% (by weight) of

boron nitride (B_4N_3) as the dopant was used. Samples before sintering were prismatic blocks with size $4 \times 4 \times 30$ mm. It was obtained by successive technological operations of forming by uniaxial pressure ($P = 40$ MPa) and pressing by high hydrostatic pressure (HHP = 400 MPa). After forming and pressing, samples were sintered in the laboratory induction furnace type HFI-25 under argon atmosphere during 1 h with an average rate of increase of temperature $5^\circ/\text{min}$. A series of samples with different sintering temperatures (isothermal holding) was obtained. Sintering temperature for various samples was ranged from 2000 to 2200°C . Morphology of fractures of samples after sintering was analyzed by scanning electron microscopy (SEM, JSM640LV). The flexural strength was determined by four-point bending on device H50KT Tinus Olsen and density—by the method of hydrostatic weighing using electronic analytical weighing-machine type ADS50. Temperature was measured using pyrometer Raytek Marathon FRICSF003H.

The crystalline structure of samples was investigated by X-ray diffraction (XRD) that was done using DRON-3 devices (Cu $K\alpha$ -radiation, Ni-filter) with the possibility of obtaining X-ray spectra in digital form. Calculations of diffraction patterns were carried out using methods specified in [10–14].

3. Results and Discussion

XRD show, in all sintered samples presence of single phase—the hexagonal α -SiC 6H, with lattice parameters $a = 3,080$ Å, $c = 15,098$ Å, and $c/a = 4,90$.

Figure 1 shows diffractograms typical for the sample at temperature of sintering 2100°C and above (On diffractograms of samples sintered at temperatures above 2100°C , deviation of maximum peak intensities from the table values can be observed). High intensities of peaks indicate an abnormally large grain size in specified temperature range.

At lower sintering temperatures from 2000 to 2080°C , intensity of peaks similar is to intensities from the initial powder α -SiC (Figures 2(a), 2(b), and 2(c)).

Data of scanning electron microscope concerning grain structure is shown in Figure 3 and data concerning strength and density are in Figures 4(a) and 4(b), respectively.

Let us consider the processes of structure formation in samples that are realized during the thermal heating. As can be seen from Figure 3(a) at 2000°C , nanopowder dispersed system (NDS) based on SiC has a uniform topology. Structural elements are homogeneously distributed in volume of sample. Increase of temperature to 2050°C according to Figure 4 causes an increase of strength (3%) and density (0,65%) of samples at practically unchanged topology of fracture (Figure 3(b)). From the point of view of the theory of dispersed systems, this fact indicates beginning of condensation recrystallization processes (hardening contacts between particles) that are realized as a result of physical and chemical reaction of system on increase of internal energy by thermal heating. Further temperature increase, according to Figure 4, leads to a sharp increase of density (on 28%) and strength (in 1,5 times) of NDS. On the fracture (Figure 3(c))

FIGURE 1: Diffractogram of SiC ceramics sintered at 2100°C , 1 h.

FIGURE 2: Diffractograms of starting powder SiC (a) and ceramic obtained at sintering temperatures 2000°C (b) and 2080°C , 1 h (c).

flattened areas that are typical for transgranular fracture are appearing. Topology becomes pronounced volume character. All of these facts are indicating the formation in the volume of so-called fracture grid that determines the mechanical properties of samples. Subsequent rise of temperature to 2100°C (Figure 3(d)) initiates the formation of large anisometric crystals that formed the dendrite skeleton of formed ceramic structure. This reduces the strength of samples at practically constant density (Figure 4). Temperature rise above 2100°C is accompanied by increase in the degree of repletion of free space in the volume of sample (Figures 3(d)–3(f)) at monotonic decrease of strength (Figure 4(b)). It should be noted fact that at temperature above 2080°C ceramic sealing does not occur, which indicates presence of closed porosity almost at the whole range of investigated temperatures.

By comparing experimental data of X-ray analysis, SEM, density, and strength curves (Figures 4(a) and 4(b), resp.), we conclude that the optimal sintering temperature is 2080°C , 1 h: at this temperature, grains size is approximately equal (Figure 3(c)), which is indicated by standard value of intensity

FIGURE 3: The topology of fractures of SiC samples obtained at different sintering temperatures: 2000°C (a), 2050°C (b), 2080°C (c), 2100°C (d), 2150°C (e), and 2200°C (f), 1 hour.

FIGURE 4: Dependence of the density (a) tensile strength and (b) from the sintering temperature of SiC ceramics.

of diffraction peaks (Figure 2(c)). This temperature corresponds to the maximum strength $\sigma = 435$ MPa in combination with a technically satisfactory density $\rho = 3,17$ g/cm³.

Let us consider processes of formation of grain structure. At temperatures below 2080°C, density and strength are low and grain structure has not been formed completely (Figures 3(a) and 3(b)); however, a small increase of sintering temperature to 2100°C leads to a sharp increase in grain size, which forms a specific grid with straight boundaries (Figure 3(d)), while the strength is reduced on ~50% at a constant density.

As can be seen from Figures 2 and 3, uncharacteristic for ceramic systems, behavior of physical and mechanical properties (Figure 4) is caused by threshold nature of grain growth process with temperature increasing. Temperature 2080°C is a critical point. At this temperature, maximum values of physical properties not only are observed, but also change the nature of nucleating process. Threshold character of SiC sintering, probably, is caused by the beginning of intense thermal diffusion.

Looking on the data in Figures 2 and 3 according to the theory of dispersed systems, it can be concluded that in investigated system up to the temperature 2080°C a heterophase spatial structure with heterogeneous type of interfacial interactions (nearby dispersed particles have individual border), which, characteristic for dispersed systems, is saved [15, 16]. Rising of temperature to 2080°C leads to an increase of interaction energy between particles.

Coagulation with preservation of phase boundaries is take place. At exceeding of given temperature destruction of interfacial contacts is beginning. The process of coagulation of nanoparticles without saving phase boundaries, accompanied by intense grain growth, occurs. The system becomes monophasic, closer to ceramic system.

Thus, from the foregoing, it can be concluded that a level of physical and mechanical properties is caused by interfacial interaction. That is, surface component of energy provides a much larger contribution to physical and mechanical properties than bulk energy.

In case of SiC nanopowders at 2080°C, limit thermodynamic state is reached. At this temperature on borders of dispersed phase, a large maximum energy is concentrated at which the strength of the bond between particles is maximum, but border still retains individuality.

Thus, due to decrease of particles size of raw material powder, it is possible to reduce the activation energy of thermal diffusion processes and carry out synthesis of SiC-ceramics under ceramic technology, but their threshold nature is the problem. At standard mode of sintering with speed 5°/min at excess of energy threshold, an intensive grain growth is occurs. Relying on experimental results of this work, it is possible to make some conclusions about possible solutions of this problem. For this we consider the sintering process from the standpoint of classical crystallography.

From the viewpoint of crystallography, grain growth in the material occurs as a result of rapid formation of a "neck" by bulk diffusion mechanism [17]. Process of collective recrystallization of grains in silicon carbide is suppressed at

temperatures above 2080°C, probably, caused by the lack of curved boundaries. As a result, at temperatures above 2080°C, within a narrow range of temperatures, (10–20°C) anomalous recrystallization occurs with high intensity. Cause of straight direct borders should be sought, in our opinion, in highly elongated hexagonal cell where the axial ratio $c/a = 4,902$ and dihedral angle of the base is $\gamma = 120^\circ$. To equilibrium configuration of borders is corresponds an orientation of three grains with apex angles 120° and it corresponds to the equilibrium surface tension forces and just such grids of boundaries with straight sides (inert boundary [17]) are formed during compacting the powder α -SiC 6H, and high temperature at sintering leads to immobilization of given configuration.

That is, threshold character of silicon carbide nanopowder sintering is associated with specificity of its hexagonal cell structure. It is possible to avoid these difficulties by applying a set of measures aimed at suppression of rapid growth, such as a significant decrease in the rate of temperature rise in the vicinity 2080°C or doping of grain boundaries by a small amount of corresponding impurity.

4. Conclusions

Given in the paper data and its interpretation allow to concluding that for the nanopowder system based on silicon carbide due to specific geometry of the elementary cell and high activation energy of diffusion processes (suppression of collective recrystallization) is characterized by

- (1) presence of a relatively large proportion of heterophase boundaries,
- (2) extreme nature of the formation of the grain structure.

Maximum strength of ceramics from SiC nanopowders is achieved with optimum grain size and strength (amount) of contacts between them. This ratio is determined by the heat treatment regime, in particular, by temperature increase rate and by temperature of isothermal holding.

The main scientific and technological task is creation of conditions for the implementation of heterogeneous crystallization. Possible solutions are to modify the thermal regime of sintering or chemical composition of solid solution of nanoparticles.

According to XRD-data (Figure 2(c)) and SEM (Figure 3(c)), at optimum temperature of sintering ($T = 2080^\circ\text{C}$), nanostructured state of obtained material is saved. This fact has a scientific interest and physical properties of consolidated nanosized SiC require further investigation. In particular, taking into account small closed porosity (Figure 4), it is possible to expect a high resistance to high-speed thermal and mechanical stresses.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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