Structure and characteristics of functional powder composite materials obtained by spark plasma sintering

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Abstract. The article describes the results of spark plasma sintering of ceramic materials based on titanium carbide, titanium carboasilicide, ceramic composite materials based on zirconium oxide, strengthened by carbon nanostructures and composite materials of electrotechnical purpose based on copper with addition of carbon structures and titanium carboasilicide. The research shows that the spark plasma sintering can achieve relative density of the material up to 98%. The effect of sintering temperature on the phase composition, density and porosity of the final product has been studied. It was found that with addition of carbon nanostructures the relative density and hardness decrease, but the fracture strength of ZrO$_2$ increases up to times 2. The relative erosion resistance of the electrodes made of composite copper-based powder materials, obtained by spark plasma sintering during electroerosion treatment of tool steel exceeds that parameter of pure copper up to times 15.

1. Introduction

Technical ceramics, due to its high hardness, wear resistance and temperature resistance is widely used in modern technology, performing a variety of functions. At the same time, production of high density ceramic materials presents a problem as sintering of the materials requires high temperatures and, in some cases, mechanical pressure, which greatly increases the cost of production. Spark plasma sintering is currently regarded as one of the fastest and most efficient way to consolidate various powder materials, including ceramic materials. In addition to the cost efficiency, spark plasma sintering has another advantage: due to the speed of the process, it can support preserving the structure of nanocrystalline structure of material.[1].

Until now, the factors hindering the expansion of application of ceramic materials has been their higher fragility, low resistance to thermal shock and mechanical unreliability. Currently the ceramic functional materials with special properties are explored worldwide. One of such materials is titanium carboasilicide, which possesses properties of ceramic as well as metal. Like metals it has excellent electrical and thermal conductivity, processability, resistance to thermal shock. The ternary titanium carboasilicide also replicates some ceramic properties: good oxidation resistance up to 1400°C and relatively low density (~4.52 g/cm$^3$). [2, 3].

It is possible to raise the fracture resistance and reliability of standard ceramics (e.g. zirconium oxide) by strengthening them using carbon nanomaterials which possess record-breaking mechanical properties. Pioneering studies on reinforcing ceramics by carbon nanotubes (CNT) have shown an increase of strength and fracture resistance, as well as changes in thermal and electrical conductivity and other properties of such composite materials [4-5].
The use of spark plasma sintering for consolidation of copper-based composite material can reduce the temperature and time of sintering and obtain a product of a given configuration.

2. Experimental procedure

To produce ceramic composite material the powder ZrO$_2$ was used, stabilized by 3 mol. % of Y$_2$O$_3$, (DeguDent GmbH), with the average particle size of 65±10 nm. The synthesis of CNT was carried out at the CVDomna system set (NanoDevice Technology, Russia) at the temperature of 650 ºС by the method of by catalytic pyrolysis of ethanol vapor (96 %) with the pressure of 15 kPa to 17 kPa. Matrix powder ZrO$_2$ was used as the carrier of Ni-Y catalyst used matrix powder. The obtained nanotubes generally are generally multilayer with a diameter less than 20 nm. Purified nanotubes were mixed with powder ZrO$_2$ in ethanol for 4 hours.

The particles of multilayer graphene were obtained by liquid phase separation of expanded graphite produced by JSC "Silur" (Perm, Russia), which was conducted with an ultrasonic disperser UZDN-2T (400 Wt, 22 kHz) in aqueous solution of sodium dodecyl sulfate. Mixing of ZrO$_2$-3Y$_2$O$_3$ powder with graphene-containing suspension was carried out in aqueous solutions of surfactant for 10 hours. Powder materials of various composition were subjected to consolidation after the mixing (Table 1).

Table 1. Composition and parameters of powder mixtures.

| № composition | Composition | The rotation speed of the mill at MA (min$^{-1}$) | Proportions of the milling body and the charging material | Environment |
|---------------|-------------|-----------------------------------------------|--------------------------------------------------------|-------------|
| 1             | 71 wt. % Ti + 25 wt. % SiC + 4 wt % graphite | 280                                           | 7:5:1                                                  | Vacuum      |
| 2             | 90 wt. % TiC + 10 wt. % SiC                  |                                               |                                                        |             |
| 3             | 80 wt. % TiC + 20 wt. % SiC                  |                                               |                                                        |             |
| 4             | 60 wt. % TiC + 40 wt. % SiC                  |                                               |                                                        |             |
| 5             | ZrO$_2$-3 mole%Y$_2$O$_3$ + (0.5-3) wt. % CNT | 160                                           | 5:1                                                    | C$_2$H$_5$OH |
| 6             | ZrO$_2$-3 mole% Y$_2$O$_3$ + (0.5-1) vol. % graphene |                                               |                                                        | SDS         |
| 7             | Cu + (25 – 37.5) vol. % Ti$_3$SiC$_2$       | 160                                           | 1:3                                                    | C$_2$H$_5$OH |
| 8             | Cu + (1-5) vol. % colloidal graphite         |                                               |                                                        |             |

Spark plasma sintering was carried out on the Dr. Sinter SPS-1050b system (SPS Syntex, Inc., Japan). The heating was conducted by passing pulsed direct current at the heating rate of 50 ºC/min to 80 ºC/min. The temperature was monitored along the outside of the graphite matrix with an optical pyrometer. The material was loaded immediately before the heating by constant load (at the pressure equal to 15 MPa and 30 MPa), which was removed after the heating. Isothermal exposure was equal to 1, 5, 10, 25 and 30 min.

The density of compact samples was determined by hydrostatic weighing. The porosity was calculated by the formula $P = (1 - \rho_{exp}/\rho_{theor}) \times 100$. The theoretical density value was calculated from the phase composition of the sintered material.

X-ray analysis of the synthesized powders and materials based on them was carried out on the diffractometer XRD-6000 (Shimadzu) in $\lambda$-Co radiation. Calculation of the phase content was carried out by the PowderCell software. Raman scattering specters were recorded with the multifunctional spectrometer «SENTERRA» (Bruker) at the emission wavelength of 532 nm. Microstructural analysis of fracture surfaces of samples was performed with scanning electron microscopes TESCAN VEGA (Czech Republic) and ULTRA 55 (Carl Zeiss, Germany).
The hardness and fracture resistance of the samples was determined by indentation of polished surface using a Vickers pyramid with a Micro Macro Vickers Hardness tester KBW 10-V (KB Prüftechnik, Germany) at the loading of 98.1 N.

3. Experimental results

Synthesis of compounds of titanium, silicon and carbon occurs during the spark plasma sintering (SPS) of mechanically activated powder composition № 1. The obtained materials is based on titanium carbosilicide Ti$_3$SiC$_2$, which quantity depends on temperature and exposure duration during the sintering. The maximum amount of titanium carbosilicide was 86 %. In addition to titanium carbosilicide the sample contained titanium carbide and a minor amount of silicon carbide.

The density of material increases with the sintering temperature increase to 1300 °C, and after that almost doesn’t change. Increasing the exposure duration also causes a small increase of density and decreases the porosity. The minimal porosity of the material based on titanium carbosilicide was 2%.

The structure of the material consists of two main structural element: titanium carbosilicide grain of lamellar structure the size of 1 µm to 10 µm and titanium carbide grain the size of 0.5 µm to 10 µm. The microstructure is non-homogeneous and contains areas of even distribution of titanium carbosilicide and titanium carbide, as well as with predominant content of one phase (Fig. 1).

![Figure 1. SEM Images of composition № 1 after SPS at 1400° C.](image1)

SPS of the compositions № 2, 3 and 4 does not lead to the formation of new compounds, the composition of sinted materials doesn’t differ from the composition of the initial charge. With increase of temperature of SPS the porosity of the compound TiC - 10% SiC decreases almost linearly. For the other compounds in the temperature range of 1100 °C to 1200 °C, the porosity remains almost unchanged, and then decreases. The compound TiC - 10% SiC sintered at the temperature of 1400 °C has the least porosity equal to 4%.

The grains of the matrix (titanium carbide) are substantially smaller than the grains of silicon carbide (ones and tens of micrometers, respectively) (Figure 2). Separate grains tightly adjoin one another, which explain the residual porosity of the material, the size of most of the pores is less than one micrometer.

The intensity of wearing of the material № 3, obtained at the SPS temperature of 1350 °C, during the testing by the “disk-block” scheme with dry friction at the pressure of 1.5 MPa equaled 3.8·10^{-9} mm wear/mm rubbing path, which is five times lower than that of silicon carbide obtained by hot pressing.

Spark plasma sintering of composite materials based on ZrO$_2$, strengthened by CNT and nanoplates of multilayer graphene, was carried out at the temperature of 1300 °C with isothermal exposure of 30 min. According to data of Raman spectroscopy the matrix of the composite materials consist of...
tetragonal ZrO$_2$. It was established that with an increase in content of CNT composite densifying processes are slowing, the shrinkage is reducing, ending for all samples at temperatures about 1100 °C. The same regularity is observed for the material with addition of multilayer graphene, but it reduces the shrinkage during sintering to a slightly greater extent than CNT. Table 2 presents the results of measurement of hardness and fracture resistance of the obtained samples.

Table 2. Properties of ceramic material ZrO$_2$-3Y$_2$O$_3$ with carbon nanostructures after the sintering.

| The content and form of the carbon nanostructures | Sintering mode | $P$ (%) | HV (GPa) | $K_{IC}$ (MPa·m$^{1/2}$) |
|-----------------------------------------------|--------------|--------|---------|-----------------|
|                                              | T (°C) | t (min) | P (MPa) |                 |
| 0.5 CNT, wt.%                                | 1350   | 120     | 0 (no SPS) | 0,9       | 12,4±0,1 | 4,9±0,2 |
| 1.0 CNT, wt.%                                |        |         |         | 0,8       | 10,4±0,1 | 7,6±0,4 |
| 3.0 CNT, wt.%                                | 1300   | 30      | 30      | 4,0       | 9,6±0,1  | 6,0±0,5 |
| 0.5 vol.% graphene                           |        |         |         | 4        | 12,0±0,2 | 5,3±0,2 |
| 1 vol.% graphene                             |        |         |         | 7        | 7,2±0,6  | 7,6±0,8 |

With the introduction of the CNT the porosity of the composite material increases and the hardness decreases, and the fracture resistance increases, especially with the CNT content equal 0.5 wt.%. The conducted electron microscopic analysis of the fracture surfaces of the sintered samples showed that the nanotubes distribution in the volume of the matrix is not uniform. In addition to CNT located in the grain boundaries, there are also areas containing agglomerates of nanotubes, the amount of which increases with an increase of their content. Apparently, the used parameters of mixing are insufficient for a homogeneous distribution of nanotubes in the matrix, which influences the properties of the composite (Figure 3, a). Introduction of graphene material also reduces the hardness of the composite ceramic matrix, particularly when the content amounts to 1 vol.%. After sintering the hardness of the composite with 0.5 vol.% graphene approaches that of pure zirconium oxide, but with an increase of content of graphene to 1 vol.% it reduced by almost a half. However, increasing the graphene content leads to increased fracture resistance. If with graphene content of 0.5 vol.% the fracture resistance of the composite and the zirconium oxide are substantially equal, the composite with 1 vol.% of graphene has the fracture resistance which is 1.5 times higher.

The graphene particles in form of plates are mostly uniformly distributed in the volume of the ceramic matrix. Among the graphene particles of uniform thickness there are quite large particles with a porous structure like a crumpled paper. Apparently, these are not completely exfoliated particles of initial expanded graphite. Such particles can serve as additional stress concentrators and reduce the positive effect on strengthening exerted by introducing graphene particles into the ceramic matrix. It should be noted that when the graphene particles consist of a quantity of layers, they are arranged in a ceramic matrix as straight plates, and single-layer graphene tends to curtail (Fig. 3, b).
After the spark plasma sintering of “copper-colloidal graphite” material at 900 °C for 5 min., the signs of formation of diamond links were detected in the graphite, consisting in the appearance of additional reflexes on the diffractogram of graphite with odd l (001) and (003) and in splitting of some existing reflexes (002), (004), (006); results are consistent with the data of authors of [6]. In [6] by intercalation of graphite with copper, which after the release of copper ions from the interlayer spaces of the graphite results in a corrugation of graphene planes with formation of \( sp^3 \) bonds. Raman spectroscopy of colloidal graphite sintered with copper confirms the formation of \( sp^3 \) bonds: a weak D4 peak appears, which indicates the presence of \( sp^3 \) bonds, the peaks G and D1 become broader, reflecting the emergence of disordered graphite, and at the G peak appears a "shoulder" D2 - so-called "the shoulder of defects", which together with D1 indicates the defects appearing at the edges and inside the graphene planes (Table 3).

Table 3. Raman specters of colloidal graphite and composite material after SPS.

| Material                    | Raman shift ( cm\(^{-1}\)) (index –Raman absol. intensivity) |
|-----------------------------|---------------------------------------------------------------|
| graphite                    | G 2D D1 D2 D4 D3 LA                                           |
| graphite                    | 1580 \( _6 \) 2682 \( _1 \) 1352 \( _4 \) no no 1510 \( _1 \) no |
| Cu -20 vol. graphite (SPS)  | 1576 \( _5 \) no 1351 \( _5 \) 1620 \( _2 \) 1230 \( _1 \) 1510 \( _1 \) no |

Energy-dispersive and X-ray diffraction analysis showed that after the sintering of the "copper-Ti\(_3\)SiC\(_2\)" material occurs a conversion of about half of the grain titanium carbosilicide to solid solution of carbon based on titanium silicide Ti\(_5\)Si\(_3\)(C) and small amounts of titanium carbide, silicon carbide, titanium silicide TiSi\(_2\) (Figure 4).
The content of silicon in the grains of titanium carbosilicide is below stoichiometric value by about 14% due to the silicon deintercalation. The electrical resistance of the composite material increased with increasing concentrations of titanium carbosilicide due to formation of solid solutions in the copper of titanium silicide with low conductivity (Table 4). The performance properties of composite materials after the SPS were better than those of pure copper due to dispersion strengthening and retaining the molten copper in the dispersed pores of carbosilicide.

Table 4. The properties of the sintered powder material "copper-Ti$_3$SiC$_2$".

| The concentration addition (vol. %) | Porosity (%) | Hardness, HB (MPa) | Flexural strength, (MPa) | Electrical resistivity resistance, (Ohm·m) | Relative erosional wear at the power, % |
|-----------------------------------|--------------|--------------------|-------------------------|------------------------------------------|--------------------------------------|
| 0                                 | 0            | 400                | 500                     | 0.021                                    | 5.6, 6.9                              |
| 0.4 graphite                      | 0            | -                  | -                       | 0.015                                    | 0.8, 3.5                              |
| 4.0 graphite                      | 3            | -                  | -                       | 0.023                                    | 0.6, 3.2                              |
| 12.5 of Ti$_3$SiC$_2$             | 2            | 650                | 280                     | 0.06                                     | 3.2, 5.2                              |
| 37.5 of Ti$_3$SiC$_2$             | 7            | 800                | 340                     | 0.14                                     | 1.0, 4.0                              |

4. Conclusion
Ceramic and metallic composite materials of various purposes were obtained by the method of spark plasma sintering; the patterns of densification, phase and structure formation were defined. It has been established that SPS allows obtaining carbon-based ceramic materials with increased wear resistance. Adding carbon nanostructures to zirconium dioxide slightly decreases the density, but increases the fracture resistance by 1.5-2 times. Electrotechnical materials based on copper with additions of titanium carbosilicide or graphite possess significantly better erosion resistance compared to copper.

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