Вісник ХНУ, серія «Фізика», вип. 24, 2016. с. 30-35

81.05.Je; 82.45.Qr; 81.15.Pq; 82.45.Yz
УДК 542.943:620.18

Synthesis by method of electro consolidation of SiC and WC, ZrO_2 nanocomposite materials with the high mechanical properties

E.S. Gevorkyan[1], G.D. Semchenko [3], M.V.Kislitsa[1],
V.A.Chishkala[2], S.R. Vovk[2], R.V.Vovk[2]

[1] *Ukrainian State University of Railway Transport, Feuerbach Square, 7, Kharkov, Ukraine, 61002*
[2]*National Technical University "Kharkov Polytechnic Institute", Frunze Street 21, Kharkov, Ukraine, 61002*
[3]*V.N. Karazin Kharkov National University, Svobody sq. 4, Kharkov, Ukraine, 61022*
[1] *edsgev@gmail.com,*[2]*r.vovk@mail.ru,* [3] *sgd@kpi.kharkov.ua,*

Application of modern ways of ceramic mater ials' consolidation and association of synthesis methods of organic and inorganic chemistry, sol-gel method and mechanochemistry, allowing to control processes of synthesis of the defined phases at molecular level, gives the chance to create highly effective composite materials.

Keywords: mechanochemistry, nanoparticles, synthesis of β-SiC, nanopowder, ZrO_2–3 wt. % Y_2O_3, WC, properties, K1C, consolidated composite materials

Застосування сучасних способів консолідації керамічних матеріалів і об›єднання методів синтезу органічної і неорганічної хімії, золь-гель методу і механохімії, що дозволяють контролювати процеси синтезу заданих фаз на молекулярному рівні, дає можливість створювати високоефективні композиційні матеріали.

Ключові слова: механохімія, наночастинки, синтез β-SiC, нанопорошки, ZrO_2–3 wt. % Y_2O_3.

Применение современных способов консолидации керамических материалов и объединение методов синтеза органической и неорганической химии, золь-гель метода и механохимии, позволяющих контролировать процессы синтеза заданных фаз на молекулярном уровне, дает возможность создавать высокоэффективные композиционные материалы.

Ключевые слова: механохимия,наночастицы,синтез β-SiC,нанопорошки, ZrO_2–3 wt. % Y_2O_3.

Introduction

The modern stage of development of science and technology is characterized by considerable achievements in the field of creation of the composite materials (CM). In modern development of high technologies the mixing of components at molecular level and creation of CM with disperse, nanosized and fibrous inclusions are the main tendencies in ceramic materials science. Therefore the mechanochemistry and sol-gel process which allow to project, create and control the properties of materials and products from them, are the most perspective directions for developing of new technological decisions and new materials with the defined properties. Results of use of the specified tendencies for creation of perspective composite materials have been presented in the report [1, 2, 3, 4].

One of the characteristics of creation method of the CM nanostrengthened by nanoparticles and nanofibres of β-SiC and Si_3N_4 is self-organization of gel structures and the purposeful organization of nanoreactors for synthesis of nanoparticles and nanofibres of the specified compounds. In nanoreactors by means of physical impacts (temperature and pressure) it is possible to operate processes of chemical transformations of tetraethoxysilane and the subsequent self-organization of radicals ($–CH_3$) in gel clusters of β-cristobalite structures into organo-inorganic complex ($–CH_3$)–$(SiO_2)_n$. This complex is a precursor of components for synthesis of nonoxygen compounds, first of all, β-SiC at low temperatures. Low-temperature synthesis of SiC, according to thermodynamic calculations [5–8], is possible only from such components as carbon and silicon monoxide.

At $P_{SiO} = 10^{-19} – 10^{-12}$ atm. and P_{CO}/P_{CO2} = 9:1 – 8:2 synthesis of SiC can be carried out at a temperature below 700 K that is confirmed experimentally [6, 7] in the course of thermodestruction of gels and modification of powders of refractory compounds for CM at their milling with silicon alkoxide. Mechanisms of low-temperature synthesis of β-SiC in the course of mechanochemical activation of powders at milling with silicon alkoxide and at heat treatment of gels on its basis are identical.

During modification of powder of any refractory filler at milling with an additive of silicon alkoxide the nucleation

and synthesis of β-SiC nanoparticles have been observed, as well as systematic and nonsystematic violations of crystal lattices of fined powders that intensify sintering of refractory powders for producing of CM.

Use of the modified by silicon alkoxide powders of α-SiC, B_4C, Si_3N_4 and Al_2O_3 as fillers of ceramic matrixes led to creation of hot-pressed crack-resistance ceramics, the corundum coatings for protection of graphite from oxidation with the intermediate layer nanostrengthened by β-SiC, nanostrengthened carbon-graphite and silicon carbide CM [9].

Use of nanoparticles of WC and partially stabilized by yttrium oxide nanoparticles of ZrO_2 allows to get by method of hot pressing at a direct transmission of current through graphite form a thin microstructure of composites with high physicomechanical properties. This process has been carried out on specially developed apparatus for hot pressing [10].

Apparatus and Procedures

Consolidation of composite materials on the basis of powders of nonoxygen compounds has been carried out by well-known method of hot pressing at temperatures of 1873–2573 K (30 min.). Hot pressing of ZrO_2 has been carried out by means of the developed apparatus of hot pressing with application of the high-ampere current at a transmission it through a graphite compression mold [10] at a temperature of 1473–1673 K and rate of temperature raise 400 degrees/min.

The phase composition of the modified powders and the developed materials on their basis, the size of grains of the synthesized phases, properties of samples have been determined by known methods. Structure of SiC materials has been studied using a polarizing microscope MIN–8 and an electronic microscope Jeol. The X-ray phase analysis has been carried out on the diffractometer DRON–3M at Cu_{Ka} radiation.

Phase structure of the received samples of ZrO_2–Y_2O_3–WC has been investigated by method of the X-ray phase analysis (the Rigaku Ultima IV diffractometer ($Cu_{K\alpha}$ – radiation, Ni – filter). For definition of exact element composition of material the X-ray spectral analysis with use of a raster ion-electronic microscope of Quanta 200 3D has been made. Definition of a form and the sizes of powders' particles has been carried out with usage of a transmission electron microscope JEM–2100.

Structure research of the sintered specimens on the basis of partially stabilized zirconium dioxide has been carried out by methods of power probe (atomic power Ntegra Aura microscope) and raster microscopy (a raster ion-electronic microscope of Nova NanoSEM). Microhardness of ceramics' samples has been determined by the automatic AFFRI DM8 microhardness tester by Vickers's method with application of 1 kg loading within 15 seconds.

Monoaxial compression tests of materials' samples have been carried out at the room temperature on the air by means of the test machine Instron 300LX.

Results and discussion

For creation of crack-resistant constructional ceramics on the basis of nonoxygen compounds have been used modified powders of these compounds during milling with an additive of silicon alkoxide (tetraethoxysilane). Nucliation and mechanochemical synthesis of β-SiC during milling of powders with this additive can be most brightly presented at obtaining of the modified electrocorundum (Fig. 1). After 1 hour of a grinding in a spherical mill mechanochemical synthesis of β-SiC in the course of milling of the organo-inorganic complex $(–CH_3)–(SiO_2)_n$ has been observed [7].

Use of the powders of refractory compounds modified by silicon alkoxide allows to obtain materials with theoretical density at much lower temperatures of their consolidation (Fig. 2).

Thanks to existence of the organo-inorganic complexes $(–CH_3)–(SiO_2)_n$ created at mechanochemical activation, mechanochemical synthesis of β-SiC nanoparticles from them and creation of β-SiC globules 80–30 nanometers in size reinforcing ceramic matrixes from modified powders of refractory compounds such as Al_2O_3, α-SiC, and B_4C, lead to increase of durability and crack resistance of these materials.

During consolidation of the modified by silicon alkoxide powders self-reinforcing of matrixes of materials by β-SiC nanoparticles, creation –intra and –inter nanostructures have been observed.

The peculiarity of structures of the materials consolidated at hot pressing from the modified powders is not only self-reinforcing of ceramic matrixes by nanoparticles that leads to their dispersion hardening, but also loss of silicate layers between grains of the modified filler (Fig. 3).

Properties of hot-pressed ceramics from the modified powders of nonoxygen compounds have been presented in Table 1.

Apparently from Table 1, figures of properties of hot-pressed materials from the powder of SiC modified by silicon alkoxide surpass values of figures of density, porosity, durability, and it provides higher rates of crack resistance and hardness at identical value of friction coefficient at comparing of properties of the consolidated materials with the usual powder of SiC.

Research of processes of hot pressing with a direct transmission of the high-ampere current of nanopowder mixes of partially stabilized zirconium dioxide ZrO_2 – 3 %Y_2O_3 and tungsten monocarbide WC have showed that the optimum modes, providing the maximum density and mechanical properties of the

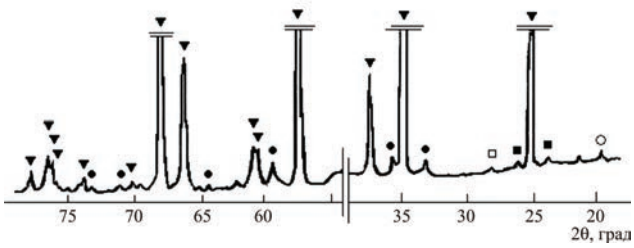

Fig. 1. Phase composition of modified fused corundum after one hour of milling: ▼ – α-Al_2O_3, ● – β-SiC, ○ – Si_2ON_2, ■ – mullite, □ – Si.

material, are: $T_{sintering}$ = 1300 – 1400 °C, $P_{pressing}$ = 30 MPa, $t_{sintering}$ = 2 min. Researches of a microstructure of the received composites ZrO_2–Y_2O_3–WC with the content in initial mixes of 10 wt. % and 20 wt. % WC that have been carried out by means of raster electronic microscopy, have showed a difference of initial mixes as well as the received materials.

As it has been shown at Fig. 3, agglomerates of tungsten monocarbide with an average size of grains are distributed in "cloud" of the white phase ZrO_2–3 wt.

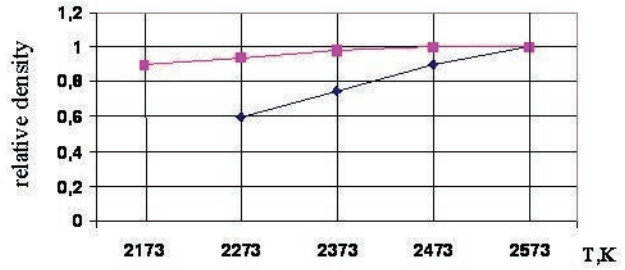

Fig. 2. Dependence of density of hot-pressed samples from usual (•) and modified powder (■) of silicon carbide.

% Y_2O_3. At this it is noticeable that in the agglomerated parts of WC there is the certain hitch similar to links in a chain which in turn chaotically coil. The microstructure of the material received as a result of hot pressing with a direct transmission of the high-ampere current at a temperature of 1350 °C has been shown in

Fig. 3. Destruction surface of hot-pressed (1850 °C, 30 min.) SiC material from the α-SiC powder modified by silicon alkoxide 1 – globules of β-SiC nanoparticles, 2 – grains of α-SiC.

Fig. 4.

From Fig. 4 it is possible to notice that grains of tungsten carbide are in the bulk located in the form of the smallest colonies of nanograins, however there are large agglomerates of tungsten monocarbide in which there are also grains of zirconium dioxide. It is demonstrably visible on the X-ray spectral analysis in point 1.

Results of properties' research of the known consolidated $(Zr_{0.94}Y_{0.06})O_{1.88}$ and developed hot-pressed ZrO_2 – Y_2O_3 – 10 wt. % WC ceramics are reported in Table 2.

From comparison of characteristics of materials from partially stabilized zirconium dioxide and the developed composite on the basis of zirconium dioxide with an additive of 10 wt. % WC it is visible that indicators of physicomechanical properties considerably increase with introduction of nanodimensional tungsten monocarbide.

Research of the influence of tungsten monocarbide nanopowders on properties of zirconium dioxide partially stabilized by yttrium oxide is currently important because tungsten monocarbide has high hardness and abrasive firmness therefore in principle introduction of these additives allows to increase wear resistance and crack

Table 1

Properties of CM from powder of silicon carbide

Properties of material	Self-bonded SiC	Hot-pressed from the modified SiC powder	Hot-pressed from the usual SiC powder
Density [g/cm^3]	3,0	3,3	2,92–3,03
Porosity [%]	2,5	0	2–5
Bending strength [MPa]	220	Not less than 650	Not more than 440
K_{1C} [MPa.m^{0,5}]	2,9–4,1	6,2–6,5	Not more than 4,4
Hardness [GPa]	9,1–9,6	14,7	10–11
Friction coefficient	0,15–0,25	0,16	0,16

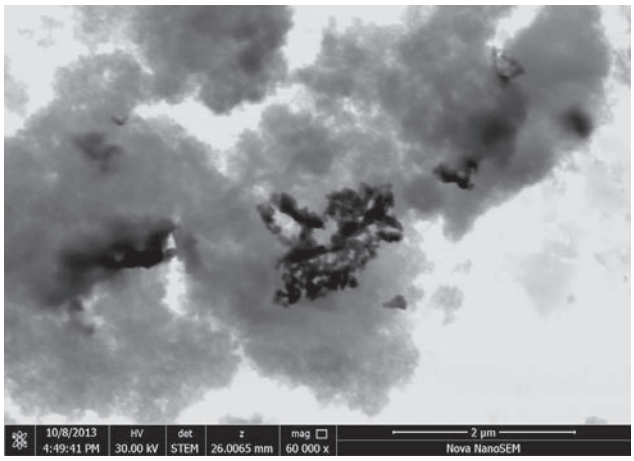

Fig. 4. Initial nanopowder mix of ZrO_2– 3 wt. % Y_2O_3 – 10 wt. % WC.

resistance of a composite as a whole.

It should be noted that tungsten monocarbide carries electric current and consequently the nanopowder mixes can put in positive dynamics into agglomeration mechanisms at hot pressing with a direct transmission of the high-ampere current. At a certain content of tungsten monocarbide in mix there will be the percolation processes, allowing to pass electric current at even rather low temperatures that in turn influences composite structurization, first of all kinetics of growth of grains. On this basis we have investigated processes of hot pressing of mixes with various content of tungsten monocarbide at various temperatures, heating speeds and exposure time, in this case pressure sustaining by graphite compression mould has been maximum.

The realized researches of hardness, durability and crack resistance of composites with various content of tungsten monocarbide give the grounds to assume that the amount of tungsten monocarbide strongly influences the hardness and crack resistance that the greatest hardness turns out at the 30 % content of WC whereas crack resistance turns out maximum at the contents 20 wt. %. Decrease in crack resistance with increase of the content of tungsten monocarbide most likely can be explained by increase in the content of W_2C.

Carbon partially penetrates into a crystal lattice of ZrO_2 that allows to increase durability on phase boundary.

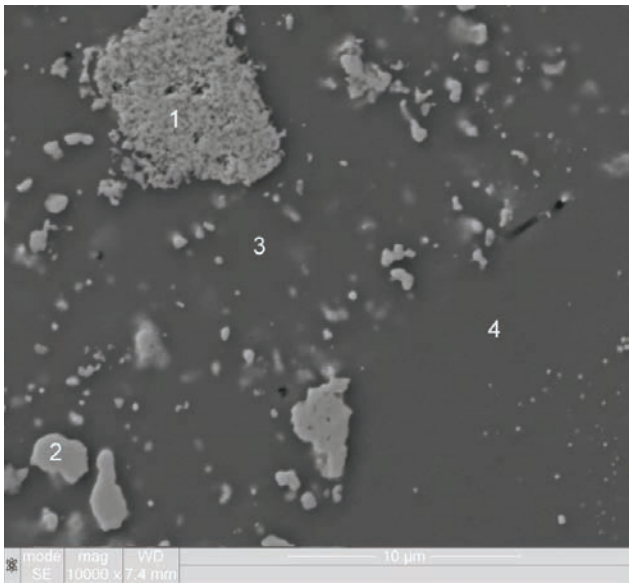

Fig. 5. Microstructure of composite of ZrO_2 – 3 wt. % Y_2O_3 – 10 wt. % WC (sintered at a temperature of T=1350 °C, P=30 MPa and hold time of 2 min.), x 10000. 1 – agglomerates of WC–ZrO_2 – 3 wt. % Y_2O_3; 2 – submicronic grain WC–ZrO_2 – 3 wt. % Y_2O_3; 3 – ZrO_2 – 3 wt. % Y_2O_3 – WC; 4 – ZrO_2 – 3 wt. % Y_2O_3.

Thus the content of W_2C decreases.

As it is shown at Fig. 6, crack extends practically bending around nanograins of tungsten monocarbide, thereby losing energy of destruction that leads to crack resistance increase.

Apparently from fig. 7 sample destruction is transgranular that points at durability on phase boundary. It is most likely explained by partial penetration of carbon from W_2C into a crystal lattice of ZrO_2 increasing durability of interphase borders that in turn increases crack resistance of a composite as well as bending strength.

As can be seen from Figure 9 with increasing hot pressing pressure shrinkage.

It adopts a smoother character.

As can be seen from the composite structure ZrO_2-3 wt.% Y_2O_3-20 wt.% WC. along with nanoparticles have submikronyye WC particles, indicating that the mechanism of nanoparticle growth heterogeneity in hot pressing by

Table 2

Properties of the hot-pressed modified zirconia ceramics

Material composition	Microhardness [HV]	Compressive strength [MPa]	Pycnometric specific gravity [g/cm^3]	Density in reference to theoretical [%]
$(Zr_{0.94}Y_{0.06})O_{1.8}$	1408	2586	6,08	98
$ZrO_2 – Y_2O_3$ – 10 wt. % WC	1650	3200	6,2	99

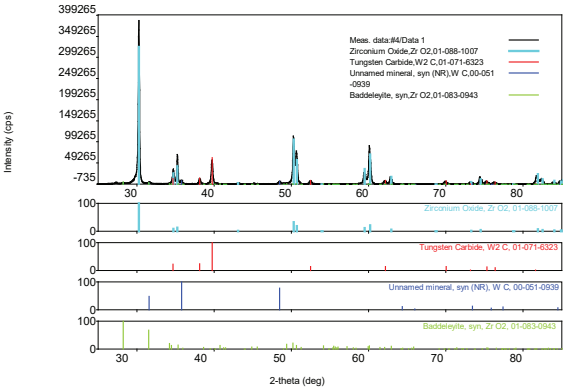

Fig. 6. X-ray spectroscopic analysis of a sample of ZrO2 – 10 wt. % WC received by hot pressing at T = 1400 °C.

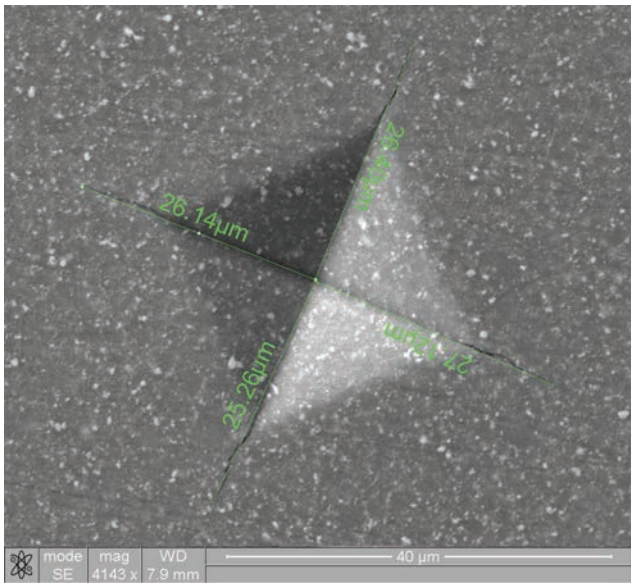

Fig. 7. Formation of cracks in a sample ZrO_2 – 10 wt. % WC received by hot pressing at a temperature T=1200 °C.

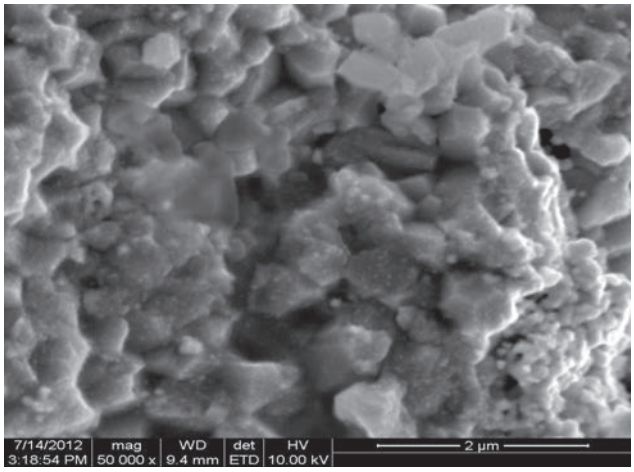

Fig. 8. Fracture of a sample of ZrO_2 – 10 wt. % WC received by hot pressing at temperature T=1200 °C and pressure P=30 MPa.

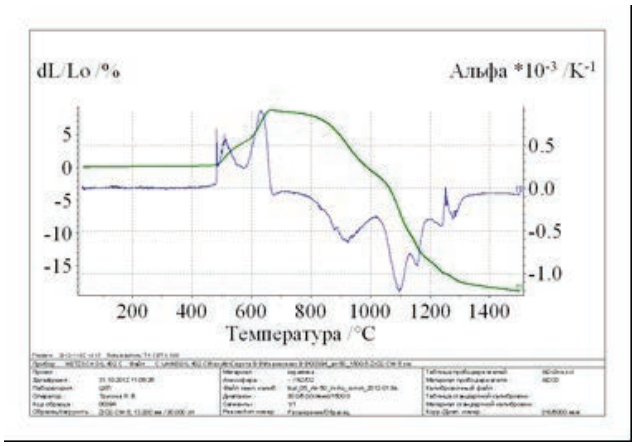

Fig. 9. Curves of composite shrinkage ZrO_2-3 wt.% Y_2O_3-20 wt.% WC shrinkage of the green line at P = 30 MPa, blue at P = 10 MPa.

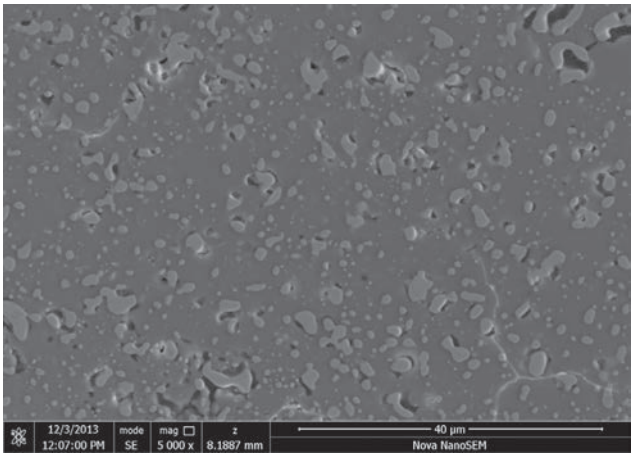

Fig. 10. Composite structure ZrO_2-3 wt.% Y_2O_3-20 wt.% WC, obtained at P = 30 MPa, the temperature T = 1400^0 C, holding time 2 minutes.

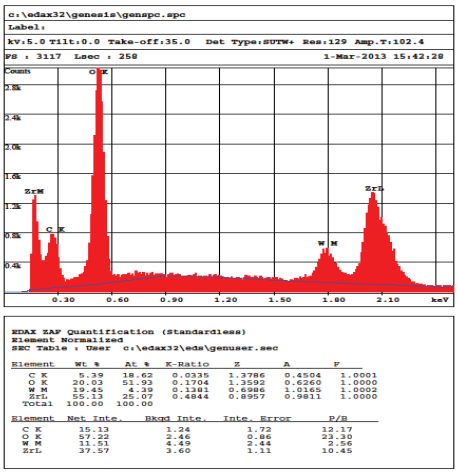

Fig.11. Chemical analysis of the elements of the composite ZrO_2-3 wt.% Y_2O_3-20 wt.% WC, received at P = 30 MPa and temperature T = 1400^0 C, holding time 2 minutes.

passing a high current direct current through the graphite mold (electro consolidation), which is located in a special vacuum chamber. Note the phase boundary between ZrO_2-3 wt.% Y_2O_3-20 wt.% and WC, which shows that the WC grains have a sleek oval surface, which suggests the possible formation of the eutectic at the boundaries between the matrix phase and a reinforcing particles.

On Fig. 10 is represented the chemical analysis of the composite ZrO_2-3 wt. % Y_2O_3-10 wt. % WC, obtained at P = 30 MPa and temperature T = 1400^0 C, holding time of 2 minutes. As can be seen, along with particles of WC, there is a small amount of W_2C, which raises the hardness of the composite, and the fracture toughness lowers.

Conclusion

Thus, mechanochemical synthesis of β-SiC nanoparticles in nanoreactors from the created organo-inorganic complex $(–CH_3)–(SiO_2)_n$ at modifying powders of refractory fillers and carbonaceous binders by silicon alkoxide and gels on its basis has allowed to create CM on the basis of SiC, B_4C, Si_3N_4 with a bending strength not less than 650 MPa and crack resistance 6,5–7,9 MPa.$m^{0,5}$.

The method of hot pressing (1200–1400 °C, the speed of temperature raise 400 degrees/min.) also synthesized the nanomaterial ZrO_2–WC from mix of the nanopowders of WC and ZrO_2 received by thermodecomposition of zirconium salts. Samples from the developed material had bending strength 250–300 MPa, crack resistance 10–15 MPa $m^{0,5}$, hardness 22–24 GPa, heat conductivity 30–35 W/m K.

From the researches carried out follows that additives of nanopowders of tungsten monocarbide to partially stabilized zirconium dioxide lead to microhardness and durability increase that, apparently, is explained by durability increase on the interphase borders and fine-grained structure of the received samples.

References

1. D.Sherman, D.Brandon, Mechanical Properties of hard materials and their relation to microstructure, Advanced Engineering Materials 1 (1999) 161–181.
2. Z.X Yuan, J.Vleugels, Biest O. Van Der, Preparation of Y_2O_3–coated ZrO_2 powder by suspension drying, J. Mater. Scien. Let., 19 (2000) 359–361.
3. Shevchenko V.Y. Technical ceramics / V.Y. Shevchenko, S.M. Barinov. – M.: Nauka, 1993.– 192 p.
4. S.M Barinov, V.Y. Shevchenko, Durability of technical ceramics, Nauka, Moscow, 1996.
5. G.D. Semchenko, I.Y. Shuteyeva, M.A. Kuschenko [and others], Thermodynamic research of possibility of low-temperature synthesis of SiC in system Si–O_2–C, All-Russian conference, Novosibirsk (2009) 187.
6. G.D. Semchenko, Constructional ceramics and refractories, Shtrih, Kharkov, 2000.
7. G.D. Semchenko, I.Y. Shuteyeva, O.N. Borisenko, Corundum coatings for high-temperature protection of graphite against oxidation Raduga, Kharkov, 2011.
8. G.D. Semchenko, Sol-gel process in technology of ceramics BI, Kharkov, 1997.
9. G.D. Semchenko, Checked by fire and time Raduga, Kharkov, 2013.
10. M.O. Azerenkov, E.S. Gevorkyan, S.V. Lytovchenko, V.O. Chyshkala, L.A. Tymofeyeva, O.M. Melnyk, Yu.G. Gutsalenko, Ukraine Patent № 72841 (2012).