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Materials Science

Development of the β-SiAlON Containing System – B_4C-SiC-Si-Al-AL_2O_3-C^{fiber} for Ballistic Protection of the Body Armour and Helicopters

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(Presented by Academy Member Ramaz Katsarava)

The goal of the work was to obtain Carbide-SiAlON ceramic composites with high impact toughness and mechanical properties. Hot pressing method was used to obtain densified materials with zero water absorption. X-ray and Spectroscopic analysis were used to study the phase analysis. The microstructure was studied by optical microscopy and electron microscopy by device Nanolab 7 ("OPTON"). The values of the electrical characteristic were calculated based on the obtained dependencies "lg p-t". The resulting composite consists of β-SiAlON matrix, silicon carbide, corundum and boron nitride nanoparticles. The obtained composite is characterized by high mechanical and service properties, which makes it suitable for ballistic protection of body armour and helicopters. © *2021 Bull. Georg. Natl. Acad. Sci.*

Composite, electron microscope, β-SiAlON

SiAlON is a general name for a large family of silicon nitride-based ceramic alloys, it was first adopted in the beginning of 1970. β-SiAlON is the most well-known phase. Its chemical formula $Si_{6-z}Al_zO_zN_{8-z}$ (z=0–4.2) and its hexagonal crystal structure are similar to the structure of β-Si_3N_4.

SiAlON is distinguished by high hardness, strength and wear resistance. It retains these properties under high temperature conditions.

Composites working at high temperatures should be characterized by high density, hardness, thermal resistance and should retain these properties when working at high temperatures. Carbide-based ceramics have a relatively high coefficient of thermal expansion, but they are oxidized easily when working at high temperatures. Because of this, science has turned its attention to obtaining the super high-strength composites –SiAlONs [1, 2]. The results of our work [3, 4] , show that the composites obtained with the SiAlON matrix are highly refractory materials with high performance

properties and retain these properties when working at high temperatures.

No special form of samples is required for this study, only a sample fracture is required. It should be noted that the fracture is better to be new, because after some time the surface of the fracture might be covered with dust particles or oxides, which reduces the contrast and makes it difficult to distinguish phases. In addition, the ions continue to move on the surface of the new fracture for some time, which makes the study very interesting.

Materials and Methods

To obtain the composites, we prepared mixtures, the composition of which is given in Table 1. To CH-10 composite we have added carbon fiber, which is characterized by high elasticity modulus (200-935 GPa), high-tensile strength (1-3GPa) and with these properties it is the desired component, since it strengthens the composite material [5].

The samples were made in a cylindrical shape by the semi-dry method, the molding pressure was 20 MPa. After drying, the samples were burned out in a sylite device at a temperature of 1450^0C. Mode 5^0C /min. At the final temperature the samples were kept for 40 minutes.

The bending strength was measured on a German-made disrupting machine R-100, which has a device determining the strength limit of the specimens on a three-point bend. The loading speed was 5 mm/hr.

When determining the bending strength limit, the maximum stress is calculated by the following formula:

$$\sigma_{\text{bend.}} = 3/2 \cdot P_{lo} / bh2 \ , \qquad (1)$$

where: P-is the force at which the sample was disrupted, kg; l_0- distance between supports at 3-point load = 25 mm; b-sample cross-section width, mm; h - the height on which the stress is applied to the specimen, mm. The test results of CH-9 and CH-10 composites are given in Table 2.

Impact viscosity was determined by the pendulum impact testing machine. When the sample is crushed, the scale marks the swing angle of the pendulum β. Impact-bending strength is calculated by the following formula:

$$A_{imp.} = A / S \ , \qquad (2)$$

where A is the work spent to crush sample, kj; S – the cross-sectional area of the samples, m^2.

For the CH-9 composite samples the cross-sectional dimensions were 1 cm x 0.35 cm; a=6.0/1x0.35=17.14 kJ/m^2; for the CH-10

Table 1. Material composition of CH-9 and CH-10 composites

	Composition of the initial component,mass%									
Composite index	Prosyanaya kaolin (Ukraine)	Al	Al_2O_3	Sic	Si	Perlite Aragats (Armenia)	Y_2O_3	MgO	B_4C	Carbon fiber
CH-9	6,5	18.0	22.0	18.0	22.0	2.0	1.5	1.0	9.0	–
CH-10	–	20.0	19.0	20.0	22.0	–	1.5	1.0	13.5	3

Table 2. The physical-technical characteristics of CH-9 and CH-10 composites

Composite name	Density g/cm^3	compression strength $\sigma_{press.}$ MPa	Bending strength $\sigma_{bend.}$ MPa	Impact viscosity a, kj/m^2	Thermal resistivity constant, $\Delta a_t(K^-)$	Thermal expansion coefficient $\alpha,10^{-6}{}^0C^-(20\text{-}700^0)$	Hv Gpa
CH-9	3,06	1840,6	261	17,14	$-5{,}7\bullet10^{-3}$	3,88	19
CH-10	2,97	2187,5	265	17,50	$-2{,}6\bullet10^{-2}$	3,80	21

composite samples the cross-sectional dimensions were 1 cm x 0.2 cm; a=3.5/1x0.2=17.50 kJ/m^2.

As can be seen from Table 2, the bending strength and the impact viscosity of both composites (CH-9, CH-10) are almost the same and amount to 261; 265 MPa and 17.14; 17.50 kj/m^2, respectively. Ceramic composites experience thermal load sand gas-thermal impacts when working at high temperatures. In all ceramic materials there are invisible micro-cracksand when the strength of the product is less than the loads, these loads are converted into the decomposition stress energy. At critical loads, high energies develop, causing decomposition of the product.

To determine these energies, Z. Kovziridze proposed a formula for calculating the failure stress energy [6]. which establishes a universal interdependence between the failure stress energy of a product, the mass of the product, and the rate of crack development under critical stress conditions. The formula for calculating the failure stress energy is as follows:

$$E_{td} = ma_{c.p}, \quad (3)$$

where E_{td} is the failure stress energy, kj; m – sample mass, g; $a_{c.p.}$ – the crack development rate –2000 m/sc.

In our case the sample dimensions were 5.2 x 5.2 x 45 mm, the sample mass was 3.86g. According to Z. Kovziridze's formula the failure stress energy is:

$$E_{td} = ma_{c.p} = 3.86 \times 2000 = 7.72kj$$

The thermal expansion coefficient of the composites (CH-9, CH-10) was determined with the help of a quartz vertical dilatometer - DKV for measuring the temperature coefficient of linear thermal expansion in the temperature range (20-700^{0}C). Table 2 shows that this indicator is the same for both composites is a = 3.88 and 3.80 • 10^{-6}, respectively.

It is known from the literature that the coefficient of thermal expansion of silicon carbide, is a = 5.18 • 10^{-6} and is characterized by high thermal resistance [7, 8].

Electrical characteristics have been established for the composite of both compositions which were obtained as a result of the "resistance-temperature" dependence experiment. The dependence of the test specimens on the "specific resistance-temperature" is linear, revealing the peculiarities that an increase in temperature causes a decrease in electrical resistance. Besides, the CH-9 specimen is characterized by lower values of electric resistance than the specimen CH-10. The values of the electrical parameters of the study composites were calculated on the basis of the obtained "lgρ- t" dependence. Three electrical characteristics were determined for both composites: the temperature coefficients of electrical sensitivity (B) and electrical resistivity (α_T) the activation energy of electrical conductivity (Ea), the value of which are presented in Table 3. The difference between the electrical characteristics was found to be significant (CH-10 composite data are approximately 5 times higher than those obtained for CH-9 composite).

The results obtained should be related to the basic phases represented in CH-9 and CH-10 composites obtained by the synthesis at 1450^{0}C, under the same conditions.

Results and Discussion

The SiAlON was synthesized in the nitrogen medium at 1400–1450^0 C, and then the obtained mass was grounded in an attritor and the consolidated composite was obtained by hot pressing at 1800^{0}C. 40 minutes, delaying at final temperature for 8 min. under 30 MPa pressure. 70 μM of study samples of the composite obtained in this mode were cut from 70mm diameter and 8 mm thick discs. The cut was made on a 395- M profile grinding machine with a 100 mm – diameter metal binding diamond cutting disc, diamond grain size 50/40μm, cutter rotation speed 4000 rpm, cutting speed 0.7 mm/min.

Table 3. Electrical characteristics values of the composites

Sample №	Coefficient of electrical sensitivity, B(K)	Activation energy of electrical conductivity, ΔE(ev)	Temperature coefficient of electrical resistance, $\Delta a_t(K^-)$
CH-10	-7170	1,24	$-2{,}6\cdot10^{-2}$
CH-9	-1560	0,27	$-5{,}7\cdot10^{-3}$

The surface of the cut specimens was ground on a 3G71 flat-bottomed grinding machine with a 200 mm- diameter diamond abrasive disc on a Bakelite binder, diamond grain size – 50/40 μm. Phase analysis of hot-pressed samples was performed on an X-ray machine DRON-3 using CuKα rays.

Examination of the X-Ray patterns of the samples burned out at 1400-1450^{0}C shows that at 1400^{0}C the characteristic reflexes of the SiAlON are already observed in both composites, and at 1450^{0}C their intensity is relatively increased. Judging by the intensity of the characteristic peaks of the SiAlON, the number of SiAlONs formed in the CH-9 composite is relatively larger than in the CH-10 composite, which can be explained by the presence of kaolin in the CH-9 composition. In our opinion, this is due to the nitrogenation of the thermo-dynamically active kaolinite core $Al_2O_32SiO_2$, which was formed as a result of the decomposition of the mineral kaolinite. The following phases have been observed in both composites: Si-Al-O-N, SiC, α-Al_2O_3, BN, and Si (small amount un reacted.).

Boron carbide in the composites was converted to boron nitride upon burning out in nitrogen medium at 1400^{0}C by the following reaction: $B_4C+2N_2=4BN+C$, which in the case of both composites is in small quantities. Newly formed, fine-grained boron nitride improves the microstructure, which is a prerequisite for high mechanical properties, such as: high thermal conductivity, low thermal expansion, good resistance to thermal shocks, easy workability, chemical inertness and low wett ability with molten metal's. It is used in radiators, boron-alloyed silicon semiconductors, welding trays, crucibles, microwave tubes, sputtering targets, high-precision welding, foundry production, etc.

Analysis performed using an optical microscope showed that the composites in both cases were silicon carbide and corundum grains located in the matrix. At the same time the microstructure of CH-10 composite is more fine-grained. It can be assumed that during the sintering process of CH-9 composite, due to the composition of these composites, more liquid phase is generated than during the sintering process of CH-10, contributing to the sintering intensity, which is evidenced by the relatively low porosity of CH-9 composite. At the same time, the liquid phase promotes the appearance of small grains and their subsequent recrystallization into large grains.

Electron microscopy shows the surface of a well-sintered specimen, on which crystals of the basic phases contained in CH-9 composites are clearly seen, namely silicon carbide and corundum grains distributed in the SiALON matrix, even the finest grains of boron nitride are also observed, which are better seen when magnified at close-up.

The micro-X-ray spectral analysis images of the CH-9 and CH-10 composites, the spectrum of the 3 sections and the scheme of the constituent elements, their percentage content, which shows that the main constituent (matrix) of the composite is SiAlON-BN.

The results of micro-X-ray spectroscopy and electron microscopy of the given composites are consistent with X-ray structural analysis. In the matrix of both composites there are represented: β-SiAlON-Al_2O_3-SiC, BN crystals are distributed in the matrix.

Conclusion

The obtained composites have been studied and determined the phase composition of the composites; in the case of both composites the main phase, i.e. the matrix is SiAlON-SiC-Al_2O_3, in which the BN grains are distributed, originated in the nitrogenation process as a result of the decomposition of boron carbide by nitrogen and the replacement of carbon with nitrogen. The composites are well sintered and the crystals are bonded together with a layer of SiAlON. Material of high physical-technical characteristics is obtained. Composite with low resistance (specific resistance approximately about 10^2 ohmxM), activation energy (E = 0.27 eV) and the temperature coefficient of electrical resistance ($\Delta\alpha$ T = 0.057 k^{-1}) with β-SiAlON matrix.

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მასალათმცოდნეობა

β- SiAlON-ის შემცველი ნანოკომპოზიტის მიღება B_4C-SiC-Si-Al-AL_2O_3-ნახშირბადის ბოჭკოს სისტემაში ჯავშანჟილეტებისა და შვეულმფრენების ბალისტიკური დაცვისათვის

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(წარმოდგენილია აკადემიის წევრის რ. ქაცარავას მიერ)

სამუშაოს მიზანს წარმოადგენს მაღალი დარტყმითი სიბლანტისა და მაღალი მექანიკური თვისებების მქონე მასალის მიღება კარბიდ-სიალონურ სისტემაში. კონსოლიდირებული კომპოზიტი ნულოვანი წყალშთანთქმით მიღებულ იქნა ცხელი წნეხის მეთოდით. კომპოზიტის ფაზური შედგენილობის შესასწავლად, გამოვიყენეთ რენტგენოსტრუქტურული და რენტგენოსპექტრული ანალიზის მეთოდი. მიკროსტრუქტურა შესასწავლილ იქნა ოპტიკური მიკროსკოპიისა და ელექტრონული მიკროსკოპიის მეთოდით "OPTON" ფირმის “Nanolab 7” დანადგარზე. ელექტრომახასიათებელ სიდიდეთა მნიშვნელობები გათვლილ იქნა "lg p-t" მიღებულ

დამოკიდებულებათა საფუძველზე. შედეგად მიღებულია კომპოზიტები β- SiAlON-ის მატრიცით, სილიციუმის კარბიდით, კორუნდის და ბორის ნიტრიდის ნანონაწილაკებით. ამრიგად, მიღებული კომპოზიტი გვიჩვენებს მაღალ საექსპლოატაციო მექანიკურ თვისებებს ჯავშანჟილეტებისა და შვეულმფრენების ბალისტიკური დაცვისათვის.

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