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ARTIFICIAL CERAMIC BINDERS BASED ON SILICON AND SILICON CARBIDE FOR SILICON-CARBIDE REFRACTORIES IN A NITRIDE MATRIX

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The main rheological and processing properties of individual and mixed binders based on SiC and Si are studied. Phase and chemical compositions, main physicomechanical characteristics, and microstructures of samples after annealing in N_2 are investigated.

Keywords: silicon-carbide refractories, artificial ceramic binders (ACBs), silicon nitride.

Ceramics based on silicon are widely used in various technology sectors owing to their specific properties [1]. Silicon nitride Si_3N_4 is a unique compound that was first synthesized by Balmen in 1844 upon heating elemental Si in N_2 released during decomposition of potassium cyanide. Si_3N_4 that was first synthesized in this manner together with silicon carbide, among others, are currently the leading refractories. The usual powder technology techniques are used to produce Si_3N_4 powders, e.g., various direct syntheses, carbothermal reduction, gas-phase synthesis and decomposition, and mechanical milling as an additional treatment [2]. Si_3N_4 features high hardness and mechanical strength, inertness to many aggressive solvents, unique electrical properties, and raw-material availability. Si_3N_4 has been widely applied as a matrix for producing silicon-carbide refractories because of these attributes.

The most common method for producing silicon-carbide items with a Si_3N_4 matrix includes adding Si to the starting mixture followed by annealing of the resulting items in an N_2 atmosphere. This forms Si_3N_4 and Si_2N_2O that bind SiC particles and allows the material to attain high physicomechanical characteristics [3 – 5]. Therefore, the chemical and physicochemical aspects of developing modern silicon-nitride materials are of great interest.

The present work studied mechanochemical synthesis of an artificial ceramic binder (ACB) based on Si and mixed suspensions based on ACBs of Si and SiC followed by nitriding of the samples via annealing in N_2. The starting material was black SiC (GOST 3647–80) and Si (Kr-0 grade) with 98 – 99% Si that was a gray powder with angular particles of maximum size 50 – 70 μm and minimal size 0.2 – 0.5 μm and the main fraction of 10 – 20 μm (Fig. 1).

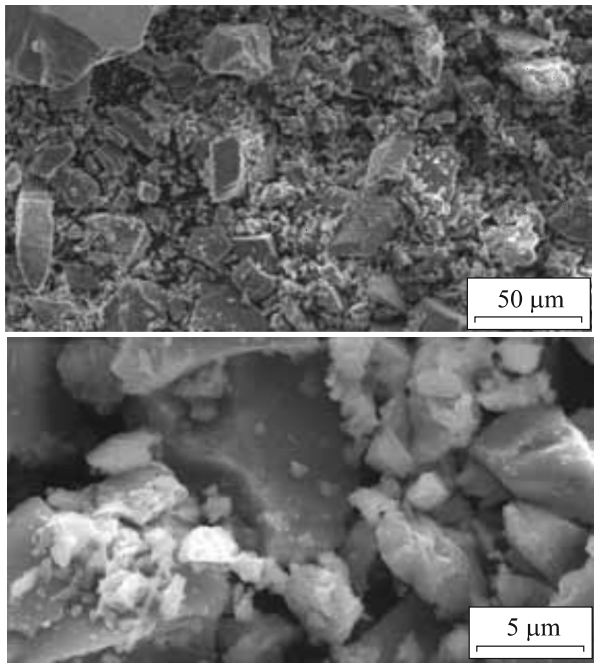

Fig. 1. Photomicrographs of starting silicon powder.

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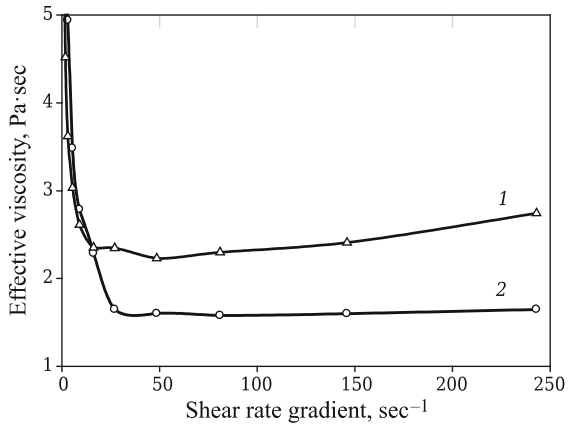

Fig. 2. Dependence of effective viscosity of SiC (*1*) and metallic Si ACBs (*2*) on shear rate gradient.

Previously, the preparation of a suspension based on Si was reported [6 – 8]. The suspension displayed thixotropic flow and a solid volume fraction C_V of 0.50 – 0.55. The binder in the present work was based on SiC [9 – 13] and Si and was produced by wet milling in a periodic ball mill via stepwise loading of the material using an organic electrolyte. After milling, the suspension was stabilized by gravitational mixing for 3 h to remove air captured during milling and to average the properties in the material bulk. The stabilized Si ACB was characterized by density 1.69 – 1.70 g/cm^3, C_V 0.53, and relative moisture 22.5 – 23.0%. The rheological properties of the SiC and Si ACBs were studied (Fig. 2). The Si suspension was characterized by distinct thixotropic flow (Fig. 2, curve *2*). The maximum thixotropic structure destruction occurred with shear rate gradient 27 sec^{-1}, which corresponded to a minimum effective viscosity of 1.6 Pa·sec. In contrast to the Si ACB, the SiC ACB possessed thixotropic-dilatant flow with minimum viscosity 2.2 Pa·sec at shear rate gradient 48.6 sec^{-1}. A microstructure analysis of Si ACB castings (Fig. 3) was consistent with significant polydispersion because of mechanical activation during milling. The average particle diameter was 2 – 5 μm. Particles of diameter <100 nm were observed on the surfaces of large particles.

The first stage of the work studied SiC ACB samples prepared by casting that were heat treated in N_2 at 1000 – 1400°C with holding at the maximum temperature for 2 h. The elemental compositions of samples after N_2 annealing at various temperatures were studied by electron-probe microanalysis using a X-MAX 50 energy-dispersive spectrometer (Oxford Instrument NanoAnalysis). The sample nitrogen content was plotted as a function of the nitriding annealing temperature (Fig. 4). This showed that increasing the nitriding annealing temperature to 1400°C increased the N content to 3.0%. This was consistent with formation of Si_3N_4 and Si_2N_2O, which started at 1100°C.

Figure 5 shows test results for the main physicomechanical characteristics of SiC ACBs annealed in N_2. The open porosity (Π_{open}) of the samples decreased insignificantly in the range 1000 – 1400°C (Fig. 5, curve *2*) and was 30.0 – 30.2%. The apparent viscosity (ρ_{app}) (curve *1*) increased by 0.5 – 1.0%. The compression strength (σ_{comp}) (curve *3*) increased considerably (by 15 – 20 times), reaching 45 – 47 MPa.

The second stage of the work studied mixed SiC–Si suspensions that were produced via mechanical mixing of separately prepared SiC and Si ACBs. The main rheological and processing characteristics of the mixed systems were studied

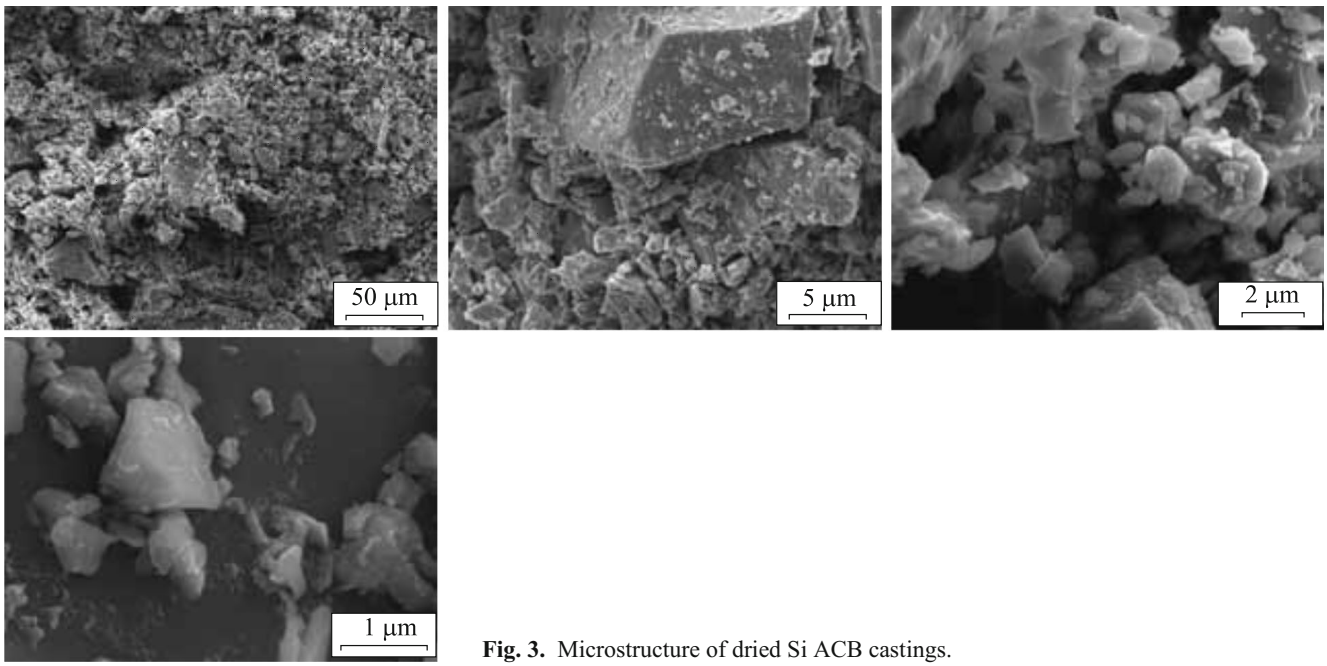

Fig. 3. Microstructure of dried Si ACB castings.

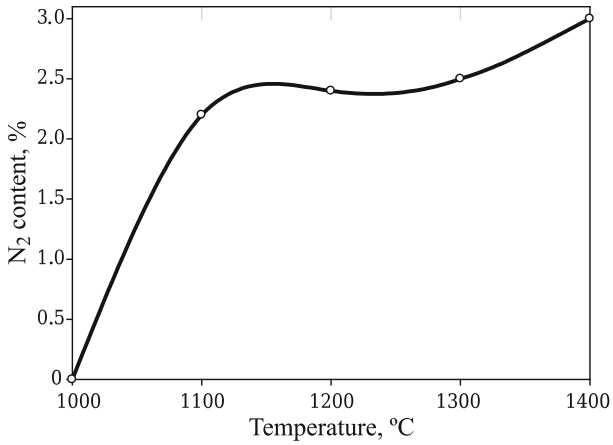

Fig. 4. Dependence of N_2 content in SiC ACB samples on nitriding annealing temperature.

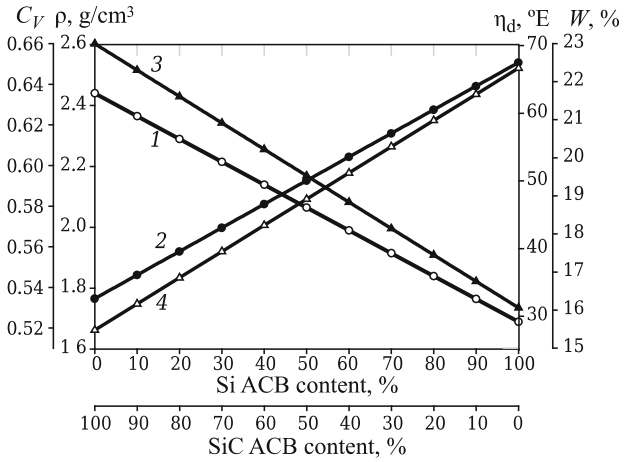

Fig. 6. Dependences of density ρ (*1*), relative moisture *W* (*2*), C_V (*3*), and dynamic viscosity η_d (*4*) of mixed SiC and Si ACBs on component contents.

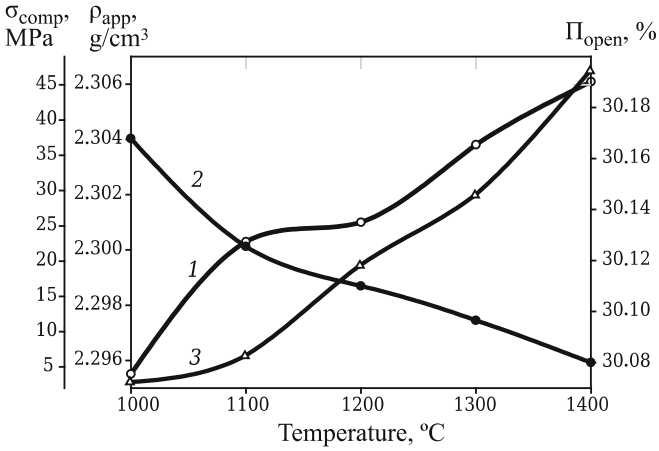

Fig. 5. Dependences of apparent density ρ_{app} (*1*), open porosity Π_{open} (*2*), and compression strength σ_{comp} (*3*) of SiC ACB samples on nitriding annealing temperature.

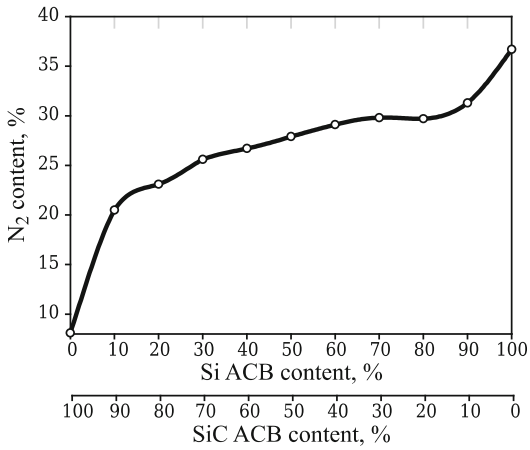

Fig. 7. Dependence of N_2 content in samples after nitriding annealing on mixed suspension compositions.

(Fig. 6). The ρ value of mixed ACBs decreased by 30 – 31% as the Si ACB content increased (Fig. 6, curve *1*) because the moisture (*W*) in the system increased (curve *2*). Also, C_V decreased by 24 – 25% (curve *3*). It is noteworthy that the system rheological properties changed unusually, concluding with a reduction of the binder mobility. This more than doubled the dynamic viscosity (η_d) (Fig. 6, curve *4*).

Castings of the mixed suspensions were preliminarily dried at 100 – 110°C and then annealed in N_2 at 1430°C with holding at the maximum temperature for 10 h. An analysis of the sample chemical compositions after annealing (Fig. 7) showed that the N concentration in the system increased by >4 times as the Si ACB content increased with a corresponding decrease of SiC ACB content. The maximum N_2 content was 36.7% for pure Si ACB. This occurred because of the formation of various Si_2N_2O and Si_3N_4 modifications, which was confirmed by x-ray phase analysis (XPA) (Fig. 8).

Photomicrographs of ACB samples after nitriding annealing (Fig. 9) showed that the material structure was fine-grained with clearly visible aggregates of Si_2N_2O and Si_3N_4 nanowires 20 – 300 nm thick that connected larger solid particles. This occurred because nanoparticles in the solid ACB that were synthesized during mechanical activation of the binder acted as activated crystallization centers.

Figure 10 shows the main physicomechanical characteristics of SiC–Si samples annealed in N_2. The sample masses increased significantly as the Si ACB in the system increased. The maximum mass increase was 45% for pure Si ACB. This indicated Si_3N_4 and Si_2N_2O with higher molecular masses than the starting composition (SiC and Si) formed extensively. The quantity Π_{open} decreased from the maximum of 30.2% by 10 – 11% (Fig. 10*a*) and reached a minimum of 26.8 – 27.0% as the Si ACB content increased to 50 – 60% and the SiC ACB concentration decreased correspondingly to 40 – 50%. Increasing the Si ACB content fur-

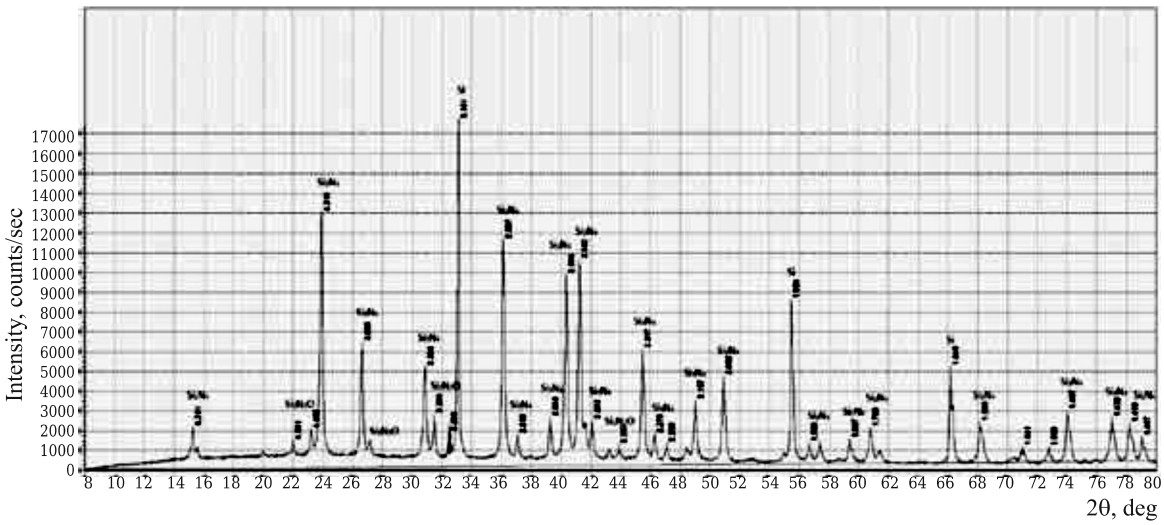

Fig. 8. X-ray diffraction pattern of 100% Si ACB samples after nitriding annealing.

ther to 100% increased Π_{open} to 29.6%. This occurred because all Si in the samples was converted to nitride compounds as a result of increasing the Si ACB content to 50 – 60%. The nitriding was incomplete if the concentration was increased further. Free Si was observed in the system (Fig. 8) and increased the material porosity. This same factor could explain the change of ρ_{app}, which decreased by 7 – 8% (Fig. 10*c*) and reached a minimum of 2.07 g/cm^3 for pure Si ACB samples, as the Si ACB content was increased over the whole range. The σ_{comp} value increased from 124 to 162 MPa (Fig. 10*d*) or by 23 – 24% if the Si ACB content was increased. This indicated that the structure strengthened by forming fibers of nitride compounds.

Thus, the specifics for preparing a polydisperse Si-based suspension with thixotropic flow were established as a result of the work. Trends in the changes of main rheological and

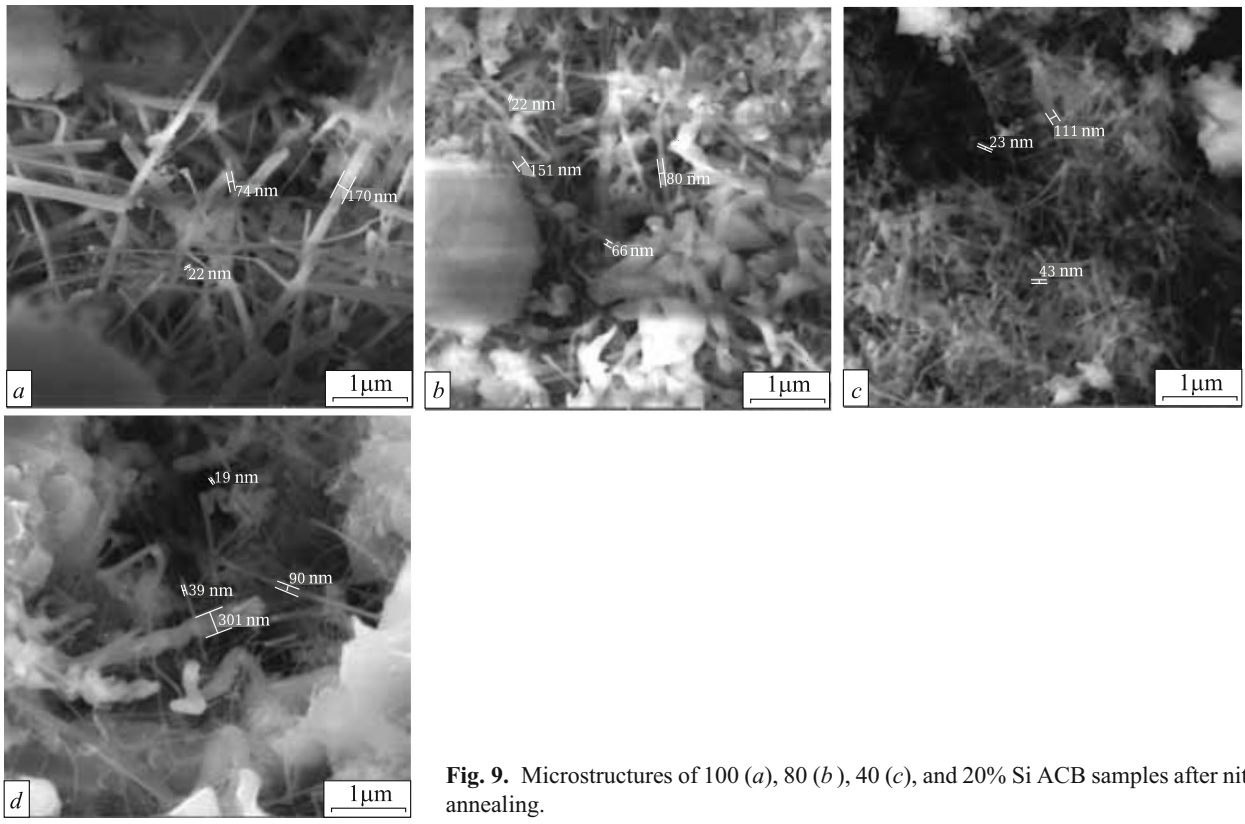

Fig. 9. Microstructures of 100 (*a*), 80 (*b*), 40 (*c*), and 20% Si ACB samples after nitriding annealing.

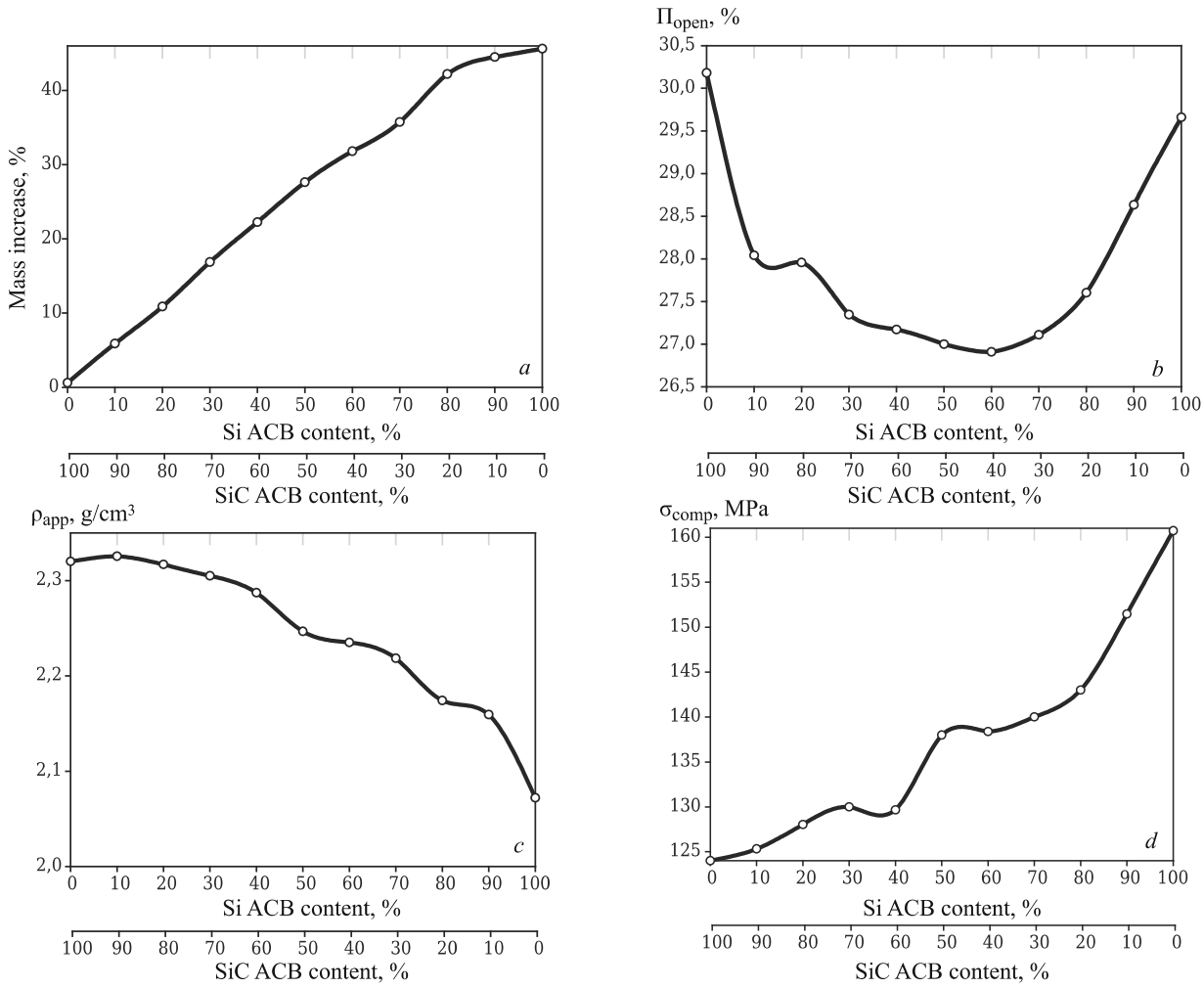

Fig. 10. Dependences of mass increase (*a*), Π_{open} (*b*), ρ_{app} (*c*), and σ_{comp} (*d*) of samples after nitriding annealing on mixed suspension compositions.

processing properties of mixed SiC and Si ACBs were found to include a reduction of density and increases of moisture and dynamic viscosity with increasing Si ACB concentration. Studies of samples annealed at 1430°C in N_2 showed that the N concentration grew to 36.7% and was associated with extensive formation of Si_2N_2O and Si_3N_4 nanowires as the Si ACB content in the mixed binder increased. Compositions of 100% Si ACB were shown to have the maximum σ_{comp} (160 – 162 MPa). Thus, the binders studied in the present work could be used to develop SiC refractories in a nitride matrix and will be reported in subsequent work.

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