Foamed silicon carbide refractories are effective heat-insulating and heat-protective materials [1, 2]. A method exists for obtaining such refractories by firing foamed ceramic blanks based on silicon carbide and silicon [3, 4] in a coke filling.

X-ray layer analysis established that the reaction sintering, evaluated with respect to the completeness of the reaction between the silicon of the starting batch and the gaseous phase is absolutely complete: there is no free silicon on the surface nor inside the product. It is found however that when fired in carbon filling large products have a heterogeneous phase composition across the cross section. In the external layers (Fig. 1a) the product of reaction of the silicon consists of the $\beta$-modification of silicon carbide and cristobalite, that is, the reaction occurs mainly with carbon monoxide according to the equation

$$3\text{Si} + 2\text{CO} \rightarrow 2\beta\text{SiC} + \text{SiO}_2.$$  

Fig. 1. X-ray patterns of foamed silicon carbide refractory with a complex bond obtained by firing in a carbon filling: 1) outside layer; 2) intermediate layer; 3) core.

Fig. 2. X-ray patterns of foamed silicon carbide with a nitride bond fired at different temperatures.
Moving deeper into the product, the content of cristobalite diminishes, but compounds develop between silicon and nitrogen; in the intermediate layer (Fig. 1b) silicon oxynitride with the formula $\text{Si}_2\text{ON}_2$ is formed, and in the center of the products (see Fig. 1b) silicon nitride, $\text{Si}_3\text{N}_4$, that is, in the reaction with the silicon nitrogen begins to get involved in the scheme:

$$3\text{Si} + \text{CO} + \text{N}_2 \rightarrow \beta\text{SiC} + \text{Si}_2\text{ON}_2,$$

$$3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4.$$

The difference in the phase composition is probably due to the presence, with the use of carbon filling in the gaseous atmosphere around the specimens, of two gases (CO and N₂), the temperature gradient across the section of the products being fired, and the different intensity of reactions (1), (2), and (3).

In order to obtain products with a uniform phase composition it is desirable to conduct reaction sintering in an atmosphere of either CO or N₂. Nitrogen is preferred as being the most available, cheapest, and nontoxic. Furthermore, upon reaction of carbon monoxide with silicon, together with silicon carbide cristobalite is formed, reducing the thermal-shock resistance of the products owing to the polymorphic inversion taking place with change in volume.

The nitrogen atmosphere forms a nitride bond which as established for dense specimens yields products of high quality [5, 7].

The synthesis of a nitride bond in an atmosphere of nitrogen involves firing porous blanks obtained by the foam method, using a mixture of silicon carbide and silicon preground together in a vibration mill. The optimum proved to be a gravimetric ratio of Si:SiC = 2:3.

With different technological parameters of the suspension (moisture content, pH, foam content) blanks were formed with different porosities. The blanks were subjected to thermal processing at different temperatures in an atmosphere of purified and dried nitrogen. The process of nitriding was controlled by x-ray analysis, and quantitative measurements of the weight increase relative to the weight of the starting silicon in the batch. Comparison of the practical weight increase with the theoretical in accordance with reaction (3) permitted, according to methods described in [8] accurate calculation of the quantity of reactive silicon and the resulting silicon nitride, that is, it enabled us to determine the phase composition of the material.

It was established experimentally that the active reaction between silicon and nitrogen commences at about 1200°. In contrast to dense specimens the porous structure of the foamed ceramics, characterizing the high gas permeability, ensures free access of nitrogen inside the specimen, as a result of which rapid reaction of it occurs with silicon and the formation of a bond of $\text{Si}_3\text{N}_4$ (Fig. 2, Table 1). At 1450° the specimen retains a very small quantity of silicon (about 2%), and the practically observable weight increase is 62%, that is, close to the theoretically possible, equal to 66.7%.

Upon completion of the reaction sintering we obtain silicon carbide material with a nitride bond, the nitride being present in the $\alpha$- and $\beta$-forms. Examination under a binocular microscope clearly reveals the fibrous structures of a new compound typical for $\alpha$-$\text{Si}_3\text{N}_4$.

Some properties of the material obtained by firing in nitrogen at 1450° using raw material containing 40% Si and 60% SiC are given in Table 2.

The coefficient of thermal expansion determined on the specimens fired at different temperatures alters from $2.56 \cdot 10^{-6}$ to $2.69 \cdot 10^{-6}$ deg⁻¹.

Deformation under load was determined by a nonstandard method since during heating in a silicon carbide furnace the phase composition of the material alters during the test because of oxidation and