Effect of the grain composition of the initial silicon carbide powder on the structure and properties of reaction-sintered silicon carbide

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Abstract. The paper shows the effect of different dispersed compositions of initial silicon carbide powders on the microstructure, strength, and crack resistance of reaction-sintered silicon carbide.

1. Introduction
Silicon carbide is a material that has an extremely wide range of properties has as high hardness and thermal conductivity, low coefficient of linear thermal expansion, maintaining the level of mechanical properties in a wide temperature range, resistance to oxidation up to the critical temperature and etc., which allows the use of SiC as materials operating in extreme conditions a significant temperature and corrosive environments [1–4]. Also, due to its good wear resistance, silicon carbide is used to produce abrasive wheels, grinding materials, plain and rolling bearings, and tools for processing heat-resistant alloys in mechanical engineering [5–7].

Materials based on silicon carbide, as well as materials based on silicon nitride, are obtained by various methods: hot and hot isostatic pressing, liquid-phase and reaction sintering. The maximum properties are achieved by using the first two methods, but due to the high energy intensity and technological complexity of production, they are not widely used [8–12].

The most technologically advanced method is reaction sintering, i.e. impregnation of a porous billet with liquid Si, by analogy with materials based on B₄C From [13–20]. This method has a number of advantages: the use of cheaper coarse powders, low sintering temperatures, and the production of virtually non-shrinkable materials, which makes it possible to produce products of complex shapes [21].

Reaction sintering of SiC materials includes: forming blanks from a mixture of SiC and carbon particles and impregnating them with liquid Si. As a result, secondary silicon carbide (SiCII) is synthesized in the intergranular space.

During sintering, silicon and carbon interact in contact (at the Si–C interface) to form SiCII at a temperature ~of 1200 °C. At temperatures above 1414 °C, silicon passes into the liquid state, dissolving carbon and saturating the silicon melt with it, up to the solubility limit of silicon in silicon carbide, after which SiC II grains begin to crystallize from the melt SiCII in the intergranular space of primary SiC particles [22, 23]. In this way, the entire pore space is filled until a dense monolithic material is obtained [24–27]. Free silicon (Si₆) or a solid solution phase based on silicon reducesits
high-temperature properties (the operating temperature of products does not exceed 1200 °C). At a temperature of 1300°C ceramic begins to soften and almost completely loses its strength at 1400 °C.

The aim of this work is to study the dependences of strength and crack resistance on the microstructure of a reaction-sintered material based on silicon carbide.

2. Materials and methods of research

Reaction-sintered ("self-bonded") silicon carbide is obtained by impregnating porous billets consisting of primary silicon carbide and carbon particles with liquid silicon, due to the dissolution of carbon and its transport through the silicon melt, and crystallization of SiCII on the surface of primary SiC particles [26, 27].

As shown in [28], it is necessary to use silicon carbide powders of different particle size distribution for maximum particle packing when forming products. The compositions of materials studied in this paper are presented in table 1. Carbon in the amount of 15 wt. % (in excess of 100 % SiC) was introduced into the material at the mixing stage of the initial components.

Table 1. Compositions of materials studied in the work

| № composition | Silicon carbide content, wt. % | Carbon, wt. % |
|---------------|------------------------------|--------------|
|               | Powder F180 | Powder M40 | Powder M5 |              |
| 1             | 80          | 10         | 10        | 15           |
| 2             | 70          | 20         | 10        | 15           |
| 3             | 60          | 30         | 10        | 15           |
| 4             | 50          | 30         | 20        | 15           |
| 5             | 40          | 40         | 20        | 15           |
| 6             | 30          | 50         | 20        | 15           |
| 7             | 20          | 50         | 30        | 15           |

The particle size of silicon carbide powder was determined on a MasterSizer 2000 laser dispersion analyzer: F180–$d_{0.5} = 95.5$ µm; M40–$d_{0.5} = 28.8$ µm; M5 – $d_{0.5} = 3.7$ µm.

Silicon carbide powders in the required ratio were mixed in a drum mixer with K-354 carbon black, the mixtures were plasticized and granulated. Samples 5×5×45 mm in size were pressed from the obtained mixtures by the method of semi-dry molding, which were dried and impregnated with silicon (silicified) at a temperature of 1500 °C in a vacuum atmosphere. Sintered samples were sent for sandblasting to remove excess silicon from the surface of the materials.

The density of the samples was determined by the method of hydrostatic weighing. Three-point bending strength was measured on a ShimadzuAG-300kNX setup. The crack resistance coefficient was determined by the Vickers pyramid indentation method on a PMT-3M microhardness meter. The microstructure was examined with a Quanta 200 electron microscope.

3. Research results and discussion

The ratios of particles of the initial silicon carbide in the materials are presented in table 1, the properties of sintered samples are shown in table 2.

Table 2. Properties of reaction-sintered silicon carbide materials

| № composition | Reaction-sintered materials | Materials, after removal of Si |
|---------------|----------------------------|-------------------------------|
|               | ρ±0,01, g/cm³ | $σ_{0±10}$, MPa | $K_{1C±0.1}$, MPa m¹/² | $σ_{0±10}$, MPa | $K_{1C±0.1}$, MPa m¹/² |
| 1             | 3.04 | 350 | 3.4 | 160 | 1.7 |
| 2             | 3.06 | 375 | 3.5 | 165 | 1.8 |
| 3             | 3.09 | 380 | 3.9 | 170 | 1.8 |
The strength of the silicon phase is approximately two times less than that of the main forming component, silicon carbide. It is natural to assume that the strength of the reaction-sintered silicon carbide should depend on the total content of Si$_f$ in the material. To check the Si$_f$ content, the samples were heat treated in vacuum at 1800 °C in order to remove (evaporate) Si, after which the effect of Si$_f$ on the strength of the materials was determined. The role of Si$_f$ as a weak link in the test material is manifested not in its total amount, but in the size and size distribution of silicon inclusions.

It is known, that the dimensions of the blank voids are directly related to the size and ratio of the particles of the formed powder. In reaction-baked silicon carbide, where the initial pores are filled with silicon, this bond is clearly visible. The number of large Si$_f$ inclusions increases in proportion to the proportional content of the largest fraction of the original silicon carbide, and the strength decreases (compositions 1–3, Table 2).

In figure 1 shows the curves of the dependence of the strength and crack resistance of the reaction-sintered silicon carbide on the amount of the coarse fraction (F180) of the initial silicon carbide in the material. Strength increases for materials obtained from silicon carbide powder upon transition to a fractional composition, which forms denser billets during molding (composition 4), and then, when less dense billets are formed, the strength decreases. Obviously, the increase in strength cannot be the result of only a decrease in the Si$_f$ content in the material, but is also explained by the smaller size of SiC grains in the structure of the material, and, accordingly, by a decrease in the size of silicon inclusions, an increase in the degree of their mutual distribution (contact area) of SiC and Si-phases (Figure 2).

![Figure 1](image.png)

**Figure 1.** Dependences of flexural strength and crack resistance for reaction sintered silicon carbide.
Figure 2. Microstructure of reaction-sintered silicon carbide (composition 4): before deleting Si\(_i\) (a), after deleting Si\(_i\) (b).

The increase in the strength of the material of composition 4 can be explained by a decrease in the size of silicon inclusions due to the filling of the gaps between large SiC particles with a fine fraction of silicon carbide particles, and, accordingly, a decrease in the total Si\(_i\) content.

Materials of compositions 6, 7 consist of a matrix of small particles of silicon carbide and large, isolated grains of silicon carbide distributed in it, the presence of which gives the structure a pronounced heterogeneity, primarily due to a significant difference in the physical properties of the matrix and grains of silicon carbide (the latter - play the role of stress concentrators). This leads to a decrease in strength and an increase in the amount of Si\(_i\).

The strength of the material of composition 4 is the highest, which is due not only to the homogeneity of the structure (Figure 2) and the small size of silicon inclusions, but also to the strength of the silicon carbide framework itself. The latter was determined on samples of reaction sintered silicon carbide after removing Si\(_i\) from them (Table 2). As seen from Fig. 1 and 3, the strength curves before and after Si\(_i\) removal are identical. The maximum strength is achieved when a framework is formed from large particles of 50 % SiC (composition 4).

Figure 3. Dependences of flexural strength and crack resistance for reaction-sintered silicon carbide after removal of free silicon.

It should also be noted that SiC powders with a grain size of less than 5 μm are not inert, they have a sufficiently large free (surface) energy and are characterized by some activity during the formation of a silicon carbide framework during sintering. This can manifest itself in the dissolution of the
The dependence of fracture toughness on the fractional composition of the initial silicon carbide differs from the dependence of strength (Table 2). For high crack resistance, polydisperse structures («viscous») should be characterized by a higher energy of destruction, i.e. the material should consist of particles of a finer fraction, therefore, with a decrease in the coarse fraction of SiC in the composition of the material, its crack resistance coefficient increases (Figure 1).

At high temperatures (above 1200 °C), the strength of the reaction-sintered silicon carbide decreases, as a result of which the entire load is taken over by the silicon carbide framework.

It is of interest to evaluate the strength of a Si-free silicon carbide framework depending on the fractional composition of the initial silicon carbide. Data on the strength and crack resistance of silicon-free samples (after removing Si from the SiC material) are given in table. 2 and figure 3. As can be seen, the strength of the silicon carbide framework largely depends on the fractional composition of the initial silicon carbide, it ranges from 160 to 170 MPa.

There is a correlation between the strength of the reaction-sintered silicon carbide before and after the removal of Si. The average strength of materials after removal of Si is 2 times lower than the strength of reaction-sintered silicon carbide.

In a silicon-free material, there is no need to spend additional energy for crack initiation, since stress concentrators are already present here in the form of pores. In addition, since the voids cannot serve as a medium for the propagation of stresses, the latter are concentrated in the silicon carbide framework. Thus, the structural strength bonds in the reaction-sintered silicon carbide are of a complex multidirectional nature.

4. Conclusions
The strength of reaction-sintered silicon carbide is characterized by high structural sensitivity. With a constant phase composition, only due to a variation in the size of the initial particles and inclusions of free silicon, the strength can change by more than 2 times. Materials with increased crack resistance are obtained from the smallest particles of the original silicon carbide. At high temperatures, the role of the supporting structural element is assumed by the silicon carbide framework, which is also highly dependent on the particle size distribution of the material.

5. References
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