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Abstract

Full Text

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On the Conditions for the Formation of Silicon in the Reduction of Silica by Carbon

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Existing ideas about the conditions for the formation of silicon in the reduction of silica by carbon are highly contradictory ([1]). This is explained by the fact that investigators judged the course of the process mainly from indirect data: loss in weight of the reactants ([2]), rates of gas evolution ([3]), etc. The statement ([4]) that silicon was detected by chemical analysis in the reduction products was not confirmed ([5]). In this connection, experiments were carried out to clarify the conditions for the formation of silicon during the interaction of silica with carbon.

The experiments used anhydrous silicic acid of chemically pure grade, fraction 0.2-0.315 mm, and graphite of grade S-4, particle size 0.063-0.1 mm. The molecular ratio of silica to carbon was set equal to 0.5, 1.0, and 2.0. Reduction was carried out in graphite crucibles. The experiments were performed in a resistance furnace with a graphite heater at atmospheric pressure and temperatures of 1600–1900° with intervals of 50°. Three crucibles containing silica and reductant mixed in the indicated proportions were placed in a furnace heated to the specified temperature and held for 5 to 120 min. The temperature was measured with a tungsten–rhenium thermocouple VR 5/20. The condensed reaction products were studied by microscopic and X-ray diffraction methods.

The experiments showed that the composition of the reaction products depends on the temperature and the ratio of the reactants.

At temperatures of 1600–1700° and $SiO_2 : C = 0.5$, the reaction product was a finely dispersed powder of silicon carbide. In a mixture with a silica-to-carbon ratio equal to 1.0 and 2.0, a sinter was obtained consisting of fused grains of SiO_2 and SiC. Raising the temperature to 1750° did not change the composition of the reaction products. The silica turned into a finely porous glass, and the silicon carbide particles became somewhat coarser. Their size reached hundredths of a millimeter.

At temperatures of 1800–1900° and $SiO_2 : C = 0.5$, only silicon carbide was likewise detected in the reaction products. At component ratios of 1 : 1 and 2 : 1, the samples consisted of quartz glass and a small amount of SiC powder.

Microscopic studies established that silicon carbide and silicon were present among the glass; depending on the duration of holding, their relative content changed. In samples held for 10 min at 1800°, only SiC was detected; with a holding time of 30 min, Si and a small amount of SiC; and with a holding time of 40 min, the silicon carbide disappeared, and only silicon remained. The silicon carbide and silicon in the glass were in close proximity, and sometimes residual SiC grains were also found inside the silicon (Fig. 1, see p. 447).

Silicon in the glass was observed in the form of globules ranging in size from hundredths of a millimeter to 2-3 mm; moreover, with increasing holding time the silicon particles became larger. The distribution of the globules was nonuniform —

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Fig. 1. Nature of the relationship between silicon carbide (gray grains) and silicon (light field). Black areas are pits. 200×

Fig. 2. External appearance of silicon beads located inside a pore of silica. 10×

Fig. 3. Silicon globules (white) in silica (gray). 200×

Fig. 4. Silicon precipitates (white) in contact with an SiC grain (gray). Dark field—silicon. 575×

···by them. The form of the silicon inclusions varied: elongated pear-shaped inclusions at the boundary with pores (Fig. 2, see p. 447) and spherical inclusions inside the glass. Around the spherical globules in the glass, radially diverging cracks filled with silicon were often observed (Fig. 3, see p. 447). The elongated form of the globules and the cracks in the glass are a consequence of the compression of still-liquid silicon droplets by the solidifying silica. If, at the boundary with a silicon droplet, there was a pore in the silica at the moment of its contraction, the silicon was partially squeezed into it. The absence of pores in contact with the metal led to the formation of cracks in the glass, which were filled with silicon.

The data presented on the nature of the distribution of silicon particles in the glass, their sizes, and their form indicate that silicon in the form of isolated droplets existed in liquid silica.

Thus, from the foregoing it follows that up to a temperature of 1750° the product of the interaction of silica with carbon is silicon carbide. Silicon is formed at an appreciable rate only at temperatures of 1800-1900°. This circumstance is consistent with the results of thermodynamic analysis of the Si—O—C system (ˆ6). The formation of silicon in this system is thermodynamically possible at temperatures above 2000° K.

The fact that, with increasing holding time at 1800-1900°, the amount of silicon carbide decreases while the amount of silicon increases indicates the formation of silicon through the interaction of SiO_2 and SiC. This was confirmed by specially

arranged experiments*, as a result of which it was established that at temperatures of 1800–1900° the interaction of silica and silicon carbide is accompanied by the formation of silicon (Fig. 4). Consequently, the direct product of the reduction of silica by carbon is silicon carbide. Silicon is formed as a result of the subsequent interaction of silicon carbide with silica.

The coexistence of silicon and silica at temperatures of 1800–1900°, as well as the coarsening of silicon particles with increasing holding time, indicates that the interaction $Si + SiO_2 = 2SiO$ developed only insignificantly under the experimental conditions.

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* The procedure for carrying out the experiments was analogous to that described.

Note: Figure translations are in progress. See original paper for figures.