The results of a thermodynamic analysis of the reduction of silicon from zircon are presented and a method for carbothermal desiliconization of zircon using arc furnace technology are proposed. Fused materials with a residual silicon concentration of 10 – 17% are prepared that can be used in the manufacture of fusion-cast refractories.

Zircon ZrSiO₄ and zirconium dioxide (zirconia) ZrO₂ are major components of the fusion-cast baddeleyite-corundum refractories that are prepared by electric melting technology in arc furnaces. In zircon, the mass ratio ZrO₂/SiO₂ = 2; therefore to maintain a ratio ZrO₂/SiO₂ of 2.8 – 3.2 as required for BK-37 and BK-41-grade refractories [1], zirconia (material rather expensive) is added to the fusion mixture.

To make the manufacture of fusion-cast baddeleyite-corundum refractories less expensive, methods were sought to prepare partially desiliconized zircon. Thus, using a fluoride decomposition method by the reaction

\[ 3(\text{ZrO}_2 \cdot \text{SiO}_2) + 4\text{AlF}_3 = 3\text{ZrO}_2 + 2\text{Al}_2\text{O}_3 + 3\text{SiF}_4 \uparrow, \]

with the properly varied zircon to aluminum fluoride ratio, one can remove an amount of silica to a fusion mixture in conformance with requirements placed on industrial baddeleyite-corundum refractories [2].

A technology for production of ZrO₂ containing 3 – 5% SiO₂ suited for baddeleyite-corundum refractories and abrasives has been developed at the Giredmet (State Research and Design Institute for Rare Metal Industry, Moscow, Russia); it is based on the chalk-assisted decomposition of zircon followed by leaching the bake produced with hydrochloric acid [3]. The TsrO-B-grade zirconia produced by this technology and commercially available from the Verkhnedneprovskii Mining and Smelting Plant (Ukraine) has been used extensively in the manufacture of baddeleyite-corundum refractories at the Shcherbinka Electrofused Refractory Plant [4].

These methods of desiliconization, however, imply a narrow specialization and for this reason have not gained wide acceptance.

Partial desiliconization of zircon can be effected by a carbothermal method using an arc furnace for melting zircon-containing fusion mixtures [5, 6].

In [7], an analysis of the high-temperature conversion of zircon and processes involved in the carbothermal reduction of zircon and silica has been given. The state diagram for the ZrO₂ – SiO₂ system is shown in Fig. 1 [8].

Zircon at high temperature develops instability and decomposes into solid dioxides of zirconium and silicon by the reaction

\[ \text{ZrO}_2 \cdot \text{SiO}_2 \rightarrow \text{ZrO}_2 + \text{SiO}_2. \quad (1) \]

At 1931 K, zircon decomposes into pure, solid-state dioxides of zirconium and silicon. In the temperature range of 1931 – 1960 K, these components persist in equilibrium. At 1960 K (eutectic temperature), a melt (SiO₂ + 4 – 5 wt.% ZrO₂) evolves. With further increase in temperature (up to a monoeutectic temperature of 2523 K), the melt, while in equilibrium with pure solid zirconia, becomes enriched in it up to 38 wt.% ZrO₂ (at a temperature slightly below 2523 K) or to 59 wt.% ZrO₂ (at a temperature slightly above 2523 K). As the temperature is raised, the melting of ZrO₂ continues to become completed entirely at 2670 K; compositionally, the liquid phase corresponds to the zircon stoichiometry (67 wt.% ZrO₂ and 33 wt.% SiO₂).

The temperature range of 1960 – 2670 K is suited for removing SiO₂ from the melt via partial or complete reduction to obtain a fused product enriched in ZrO₂.
The reduction of silica from zircon via carbon can be described as

\[ \text{SiO}_2 + 2C = 2\text{CO} + \text{Si}, \] (2)  
\[ \text{SiO}_2 + C = \text{CO} + \text{SiO} \] (3)

to yield either silicon by reaction (2) or gaseous silicon monoxide by reaction (3). Side reactions (preferably avoided) leading to the formation of carbides may intervene in the process of reduction.

The carbon-assisted reduction of silica to silicon monoxide can be described by reactions (4) and (5), and to silicon — by reactions (6) – (8), on assumption that no solid solution has been formed:

\[ \text{SiO}_2 (\text{solid}) + C (\text{solid}) = \text{SiO} (\text{gas}) + \text{CO} (\text{gas}), \] (4)  
\[ \text{SiO}_2 (\text{liquid}) + C (\text{solid}) = \text{SiO} (\text{gas}) + \text{CO} (\text{gas}), \] (5)  
\[ \text{SiO}_2 (\text{solid}) + 2C (\text{solid}) = \text{Si} (\text{solid}) + 2\text{CO} (\text{gas}), \] (6)  
\[ \text{SiO}_2 (\text{solid}) + 2C (\text{solid}) = \text{Si} (\text{liquid}) + 2\text{CO} (\text{gas}), \] (7)  
\[ \text{SiO}_2 (\text{liquid}) + 2C (\text{solid}) = \text{Si} (\text{liquid}) + 2\text{CO} (\text{gas}). \] (8)

Using thermodynamic constants from [7], relationships \( \Delta G^0_T \) versus temperature were calculated for these reactions. The temperature intervals considered were: (i) below the silicon melting point (1686 K); (ii) from the silicon melting point 1686 K to the silica melting point 1986 K, and (iii) above the silica melting point (> 1986 K). The calculated values of \( \Delta G^0_T \) for reactions

\[ \text{SiO}_2 (\text{cond}) + C (\text{solid}) = \text{SiO} (\text{gas}) + \text{CO} (\text{gas}), \] (9)  
\[ \text{SiO}_2 (\text{cond}) + C (\text{solid}) = \text{Si} (\text{liquid}) + 2\text{CO} (\text{gas}), \] (10)

are shown plotted in Fig. 2. In curves 9 and 10, the state \( \text{SiO}_2 (\text{cond}) \) corresponds to states \( \text{SiO}_2 (\text{solid}) \) and \( \text{SiO}_2 (\text{liquid}) \).

An analysis of the relationships \( \Delta G^0_T = f(T) \) calculated for the above temperature intervals shows that at \( T < 1686 \) K, reaction (4) is strongly shifted to the left. As liquid silicon becomes produced in the system at 1686 K, the reaction (4) in the temperature range of 1686 – 1986 K intensifies strongly, and the value of \( \Delta G^0_T \) for this reaction becomes zero at 1955 K (see Fig. 2, curve 9, reaction (9)). Reaction (5) for carbon-assisted reduction of liquid silica is strongly shifted to the right, and displays \( \Delta G^0_T < 0 \) over the entire temperature interval.

For silica reduced to silicon by reaction (6), the calculated values of \( \Delta G^0_T > 0 \), and over the entire temperature interval of up to 1686 K, this reaction is strongly shifted to the left. In the temperature range of 1686 K < \( T < 1986 \) K, for reaction (7), \( \Delta G^0_T \) is 0 at 1848 K and then assumes a negative value, that is, reaction (7) is strongly shifted to the right. At \( T > 1986 \) K, \( \Delta G^0_T \) for reaction (8) is less than zero at any temperature (see Fig. 2, curve 10, reaction (10)). It is seen therefore that the temperature at which liquid silicon evolves