Formation of Impurity Inclusions in Silicon when Smelting in Ore-Thermal Furnaces

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Abstract. Silicon production by carbon reduction of silica-containing raw materials is performed in ore-thermal furnaces. The process proceeds at high temperatures (above 2,000°C). Consumers place high demands on the chemical purity of the silicon smelted, but the finished product contains a negligible amount of impurities. We have analyzed the causes for the impurity inclusions in silicon forming in smelting based on the data on the behavior of various elements penetrating the process with quartzite and reducing agent ashes. The chemical composition of furnace slag and silicon samples from the Silicon JSC of RUSAL (Russia) has been analyzed using various techniques, i.e. metallographic, X-ray fluorescence, X-ray diffraction, and X-ray spectral microanalysis. It has been established that the main source of non-metallic inclusions in silicon are furnace slag particles enmeshed in the melt when it is released from the tap. Due to the high degree of iron passing into the melt when smelting, the main metal inclusions are metal aluminum solutions based on iron, silicon, and other elements: FeSi$_{2}$Al$_{0.3}$, FeSi$_{1.5}$Al$_{0.3}$, and FeSi$_{2}$Ti. The main way to improve the smelted silicon quality is to select feed with a minimum amount of impurities and conduct the process at optimal temperatures in the quartzite melting zone.

1. Introduction
The metallurgical industry is an integral part of the developed world countries, including Russia [1, 2]. The production of metallurgical silicon (Si$_{met}$), which is used as a deoxidizer in the cast iron manufacture, a modifier of the alloy properties, an alloying element in alloys, and a feedstock to produce polycrystalline silicon, organosilicon materials, and silanes [3–7], is developing due to expanding the raw material base by involving new ore and man-made feeds and improving the process [8–14]. The global Si$_{met}$ production reaches ~1 million tons per year; the largest producing country is China. The Norwegian Elkem Concern is the second-largest silicon manufacturer. In Russia, the largest metallurgical silicon manufacturer is Silicon JSC of RUSAL.

2. Research Objective
Silicon is obtained in ore-thermal furnaces (OTF) from silica-containing raw materials by reduction with carbon in the main reaction [4, 8, 15, 16]:

$$SiO_2 + 2C = Si + 2CO.$$  

Quartzite is mixed with a mixture of carbonaceous reducing agents, and the resulting charge is loaded into an OTF. In the furnace, silica is reduced in the following stages: the SiO formation due to the silica
evaporation in a reducing atmosphere, the interaction of SiO$_2$ with carbon to form SiC, and the interaction of SiC with silica and SiO to form elemental silicon. Due to the inevitably forming intermediate compound - gaseous silicon monoxide - the target product extraction is 70–74%.

To obtain a marketable product meeting the consumer requirements, the silicon smelted should contain minimum impurities (Fe, Ca, Al, Ti, etc.). At Silicon JSC, the charge for silicon production consists of quartzite obtained from the Cheremshansk deposit, being the enterprise’s ore base, and a mixture of carbonaceous reducing agents (CRA): charcoal, petroleum coke, and coal from various deposits. The research objective was studying the behavior of the charge components when melting in OTF to analyze the mechanism of forming impurity inclusions in smelting products - silicon and slag from Silicon JSC.

3. Impurities Penetrating the Carbothermic Process

The choice of silica-containing feed for silicon smelting has very stringent requirements for chemical purity since most of the impurity elements penetrate the smelting process with the ore part of the charge (55% Fe, 9% Ca, 60% Al). The Cheremshansk quartzite, the deposit of which is represented by a bed of monomineral quartz sandstones, has the following composition, % wt.: SiO$_2$ – 98.75–99.46 (average 99.2), Fe$_2$O$_3$ – 0.14; CaO – 0.03 and Al$_2$O$_3$ – 0.37. Due to the stable crystal lattice, quartz usually does not contain a large amount of structural impurities. According to [17], the main share of impurities falls on monovalent (K, Na, Li) and divalent (Ca, Mg, Ni, Cu, Cr) alkaline earth cations, but additionally, they also include trivalent (Fe, Al) and tetravalent (Mn, Ti, Ge, etc.) atoms. Also, impurities penetrate the process with CRA ash. Along with chemical purity, CRA should have satisfactory reactivity to ensure the reduction in OTF. Depending on the origin, each carbon material differs in ash content and reactivity (Figure 1). In this regard, in industrial production, a mixture of active but expensive charcoal, low-ash low-reactivity petroleum coke, and hard coals produced in Russia, Kazakhstan, and Colombia (these materials are characterized by average ash content and reducing properties) is used.

![Figure 1. Comparison of the Carbonaceous Reducing Agent Properties](image)

4. Results and Discussion

We have studied the silicon and furnace slag samples from Silicon JSC. The Simet samples have been taken under the normal operating mode of OTF No. 6 (25 MVA capacity), and the slag samples from the taphole during the scheduled repair of the furnace. The chemical composition of samples has been studied by metallographic, X-ray fluorescence (XRF), X-ray diffraction, and electron microprobe analysis (EMPA) techniques.

Silicon production is considered slag-free, unlike similar ferroalloy production processes, but a small amount of slag is formed during carbothermic smelting (up to 5 % in high-power smelting and 2–3% in small and medium-sized furnaces), which reduces silicon extraction by an average of 2.2 and 1.2%, respectively).

The source of non-metallic inclusions in Si$_{net}$ is slag particles enmeshed in the melt when it is released from the tap, that further crystallize reducing the finished product quality. Metallographic
analysis has been performed using an Olympus GX-51 microscope (Olympus, Japan) equipped with an Altera20 digital camera. XRF has been performed using an S4 Pioneer spectrometer (Bruker AXS, Germany).

According to the studies, furnace slag contains intermetallic compounds and silicon inclusions, but to a greater extent - refractory oxygen-containing phases with a complex composition (as a result of the under-reduction of their oxide elements, including crystalline and amorphous silica). Also, the samples contain silicon carbide as a result of intermediate high-temperature interactions between silica and a reducing agent (according to the X-ray diffraction analysis performed using a DRON-7.0 diffractometer with Cu-Kα radiation on a nickel filter, the average Si content in slags is 44.1% wt).

![Figure 2. Furnace Slag of Silicon Production: a – general view of the sample; b – metallographic analysis (dark area); c – the XRF result.](image)

We have also performed EMPA of Si$_{inert}$ samples using a Superprobe JXA-8200 electron probe analyzer (Jeol Ltd., Japan) (Figure 3, Table). Photos of the backscattered electron images of the samples under study (COMPO mode - atomic number contrast, TOPO mode - topographic contrast) have been taken using a scanning electron microscope, and the phase chemical composition determined using an energy-dispersive spectrometer. Measures to prepare a sample for metallographic studies included cutting samples using a Labotom-5 cutting machine (Denmark), pressing samples into the DuroCit resin to prepare samples for grinding, grinding and polishing the sample surface using a Tegramin-25 grinding and polishing machine (Denmark), and etching the sample surface with an etchant of the following composition: 90 ml H$_2$O+5 ml HNO$_3$+5 ml HF.

According to the studies, the main inclusions in Si$_{inert}$ after smelting are intermetallic compounds, mainly silicides – FeSi$_2$Al$_{0,3}$, FeSi$_{1,5}$Al$_{0,3}$ (with Ti impurity), and FeSi$_2$Ti (with Al impurity). The presence of Zr in inclusions is also confirmed by XRF since as a lining component, this element can penetrate the melt and intermetallic compounds. Non-metallic inclusions are oxygen-containing phases.

5. Analysis of Forming Impurity Inclusions in the Finished Product

The main aluminum supplies are related to corundum Al$_2$O$_3$ contained in quartzite (sometimes the OTF is fed with kaolinite Al$_2$O$_3$-2SiO$_2$-H$_2$O, which decomposes when heated to 1,250°C with the formation of mullite 3Al$_2$O$_3$:2SiO$_2$). The reduction of aluminum from its oxide occurs through the stage of forming stable aluminum oxycarbides. Mono-oxycarbide Al$_2$OCC decomposes in a peritectic reaction with the formation of aluminum metal (Al$_2$OC ↔2Al + CO), and in the high-temperature zone (above 2,000°C), aluminum mono-oxycarbide can be reduced to form aluminum carbide (Al$_2$OC + 3C = Al$_4$C$_3$ + 2CO). Aluminum carbide is reduced to silica at a temperature above 2,000°C (2Al$_4$C$_3$ + 3SiO$_2$ = 8Al + 3Si + 6CO).

In the presence of iron, silicon, copper, nickel, or their oxides, Al$_4$C$_3$ can interact with them to form metallic aluminum solutions based on iron, silicon, and other metals [19]. This can explain the high content of this impurity in silicon.
According to the results of summarizing numerous analytical production data, various authors believe that \( \sim 50\text{–}88.7\% \) of aluminum passes into silicon smelted [4]. According to the latest data published, this figure is taken equal to 89\% [20].

From the presence in the finished product point of view, one of the most problematic impurities is iron, which penetrates the OTF as hematite Fe\(_2\)O\(_3\). In the presence of a gaseous reducing agent CO, it transforms into FeO while forming elemental Fe and CO\(_2\). Iron carbide formed at 700\text{–}800\degree\text{C} (3\text{Fe} + \text{C} = \text{Fe}_3\text{C}) is spent to form aluminum oxycarbide and elemental iron by interaction with alumina. Elemental iron dissolves at high temperatures and therefore, is accumulated in the finished product. From iron oxide, the metal is reduced even at a temperature above 950\degree\text{C} (\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2)\).

The iron has a beneficial effect as it easily destroys SiC and interacts with SiO, thereby contributing to a shift of the reaction toward silicon formation but forming silicides (\text{Fe} + n\text{SiC} = \text{FeSi}_n + n\text{C}; 2\text{Fe} + \text{SiO} = \text{FeSi} + \text{FeO}) [21].

When using materials with high iron content in the charge, the charge melting, rather than reduction processes develop first, which leads to the under-reduction of silica [22]. Therefore, ingress of feed with
a significant content of iron-containing minerals into the process should be avoided; from this point of view, one of the ways to prepare feed for smelting is the magnetic separation of quartz grains.

The degree of Ca passing into the melt varies within a wide range (36–84% [4]) and depends mainly on the charge material composition and the operating mode. Calcium can penetrate the process with quartzite minerals: diopside, sphene, and limestone. In OTF, along with the reduction of silica, partial reduction of impurities from the reducing agent ash CaO occurs. During the smelting, part of calcium evaporates, passes into the reaction gas, is blown out of the furnace, and released as CaO dust. Part of gaseous CaO reacts with under-reduced silica to form silicates at 2,130°C (2CaO + SiO₂ = 2CaO·SiO₂).

Under-reduced CaO together with alumina and silica forms complex refractory composite oxides (slag phase), which deteriorate the Siₘₜₐ grade. Thus, to reduce the Ca passing into silicon, it should be transferred into the gaseous state to a maximum extent, and hardly decomposable complex silicates should not be allowed to penetrate smelting.

Titanium penetrates the process as sphene, rutile, and ilmenite. According to [21], the ilmenite reduction sequence in the Si–O–C system is as follows:

\[ \text{FeTiO}_3 \rightarrow \text{TiO}_2 + \text{Fe} \rightarrow \text{Ti} \rightarrow \text{TiC}. \]

Magnesium penetrates OTF as oxide (less commonly – magnesioferrite MgFe₂O₄). Magnesium forms stable silicide with silicon Mg₂Si. The degree of this impurity passing into silicon is taken equal to 10–35% [20].

6. Conclusions
According to studies, the main impurity inclusions in Siₘₜₐ are represented by intermetallic compounds based on metal solutions of aluminum with iron silicides. The presence of aluminum carbide indicates the incompleteness of the recovery process. Silicon production slag is mainly composed of refractory compounds based on under-reduced metal oxides penetrating the process with a charge. When silicon is released from OTF, the slag is enmeshed in the melt, which causes the presence of non-metallic inclusions in the finished product. The main way to improve the quality of silicon smelted is to select feed with minimum impurities and conduct the process at optimal temperatures in the silica melting zone.

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