A study on reduction processes of elements in the system $\text{V}_2\text{O}_5$-$\text{Si}$

M A Golodova$^1$, I D Rozhihina$^2$, O I Nokhrina$^2$ and I A Rybenko$^3$

$^1$Institute of Fundamental Education, Siberian State Industrial University, 42 Kirova Street, Novokuznetsk, 654007, Russia
$^2$Institute of Metallurgy and Material Science, Siberian State Industrial University, 42 Kirova Street, Novokuznetsk, 654007, Russia
$^3$Institute of IT and Automation Systems, Siberian State Industrial University, 42 Kirova Street, Novokuznetsk, 654007, Russia

E-mail: golodova_ma@mail.ru

Abstract. The calculation of parameters of elements reduction in the system $\text{V}_2\text{O}_5$–$\text{C}$–$\text{Si}$ was made at temperatures of metallurgical processes by the method of thermodynamic simulation. Dependences of vanadium reduction from its oxides with carbon and silicon oxides separately with each reducing agent, as well as in combination, on the temperature and reducing agents consumption were considered. The obtained results led to the conclusion that the vanadium reduction from vanadium pentoxide in combination with carbon and silicon takes place with the predominant formation of vanadium compounds: vanadium carbide and vanadium silicides, the main reductant is carbon.

1. Introduction
Currently, the actual problem is a complex usage of primary and secondary raw materials in the iron and steel industry. Extraction of components – valuable alloying additives from such materials can improve the production efficiency and at the same time the products quality. Among the most needed alloying elements, the introduction of which can significantly increase the metal performance properties, is vanadium [1-3]. The basic alloying material in the manufacture of vanadium-containing steels is high-priced ferrovanadium. For the further expansion of production and competitiveness assurance of vanadium-containing steels the alloying method, based on the metal processing by oxide vanadium-containing materials including a converter vanadium slag, has a special importance, while ensuring the conditions for vanadium reduction from these materials.

Currently, aluminum, silicon, calcium of high value are used as reducing agents. In this regard, the development of steel processing technology by converter vanadium slag with application of silicon and carbon as reducing agents is an urgent task. Low value of carbon application would significantly reduce the cost of steel products. However, to determine the optimal parameters for carbon-silicon thermal reduction of vanadium from converter vanadium slag the comprehensive examination of processes, including reduction of vanadium pentoxide with carbon and silicon, should be performed.

2. Research and results
The aim of this study was to consider the processes taking place during vanadium reduction with carbon and silicon, as well as vanadium pentoxide reduction with each reducing agent separately and in combination.

Currently, thermodynamic simulation is widely used to study elements reduction from the oxide systems [4-6]. The problem solution targeting determination of conditions for vanadium reduction in the system \( V_2O_5 \)–nС–mSi was performed with the use of methods of thermodynamic modeling based on the equilibrium conditions calculation in the model thermodynamic systems. While implementing the thermodynamic simulation, a ready software complex “Terra”, developed in Moscow State Technical University, was used. On the basis of maximum entropy principle it finds the equilibrium composition of a multicomponent heterogeneous thermodynamic system for high temperature conditions [7].

The process research was carried out by solving model problems for determination of the conditions for vanadium reduction in the systems, the input flow of which consists of a combination of elements V–O–C–Si, represented by a group of substances \( V_2O_5 \)–nС–mSi, where n and m – mass of carbon and silicon per 1 kg of vanadium pentoxide. The initial composition of the system was formed by specific values of the parameters n, m.

At the first stage of calculations the possible compositions and the boundaries of concentration areas of reduction processes flow were identified, as well as the temperature influence on these parameters. The list of substances, that can be formed from the given elemental composition of the mixture for temperature range from 1573 to 2273 K, were determined by numerical simulation using the software package “Terra”. Thermodynamically the possible quantity of substances, generated from the indicated elements for a selected temperature range, was approximately 20. All concentration values of the substances in the final state were divided into significant and insignificant with a difference threshold 10-4 mol/kg of the mixture. The significant substances were the condensed phase consisting of \( \text{C}, \text{V}, \text{VC}, \text{VO}, \text{V}_2\text{O}_4, \text{V}_2\text{O}_3, \text{Si}, \text{SiO}_2, \text{SiC} \) and vanadium silicides and a gas phase consisting of \( \text{CO}, \text{CO}_2, \text{SiO} \).

To investigate the temperature influence on vanadium reduction process in the system \( V_2O_5 \)–С–Si the calculations of equilibrium states at temperatures from 1673 K to 2273 K were made. The minimum and maximum temperatures were conditioned by the temperature values characteristic to the out-of-furnace steel treatment, and vanadium melting point 2173 K. The calculation results are presented in Figure 1.

Analysis of the results showed that the vanadium reduction process from its oxides does not dependent on the temperature in the range from 1673 to 2073K. The total mass of vanadium oxides in the reaction products at a temperature below 2073 K goes to zero during the increase in the carbon consumption from 0 to 0.5 kg/kg \( V_2O_5 \), during increase of silicon consumption from 0 to 0.7 kg/kg \( V_2O_5 \). The vanadium reduction process from vanadium pentoxide in the system \( V_2O_5 \)–С ends at a specific carbon consumption 0.5 kg/kg \( V_2O_5 \), and the system \( V_2O_5 \)–Si – at a specific silicon consumption 0.7 kg/kg \( V_2O_5 \).

Condensed and gas phases were selected for a better study of the vanadium reduction in the process products. The analysis of these phases was performed.

The composition of the condensed phase comprises vanadium oxides, carbide and vanadium silicides, silicon carbide, silicon dioxide, metallic vanadium, carbon and silicon. The gas phase, formed during the vanadium oxides reduction, consists of reaction products of vanadium oxides reduction with carbon and silicon (\( \text{CO}, \text{CO}_2, \text{SiO} \)) and dissociation product of vanadium oxides – \( \text{O}_2 \).

Results of thermodynamic calculations for the system \( V_2O_5 \)–С–Si are shown in Figures 2 and 3.

From these dependences it follows that the mass of the condensed phase (Figure 2a) increases with the increase of silicon consumption and decreases with the increase of carbon consumption. For the gas phase (Figure 2b) the relationship is reverse.

As can be seen from the curves in Figure 3 the basic component of the gas phase is carbon monoxide. Its mass increases with the increase of carbon consumption and decreases with the increase of silicon consumption. SiO mass increases with the increase of carbon consumption, while at the
increase of silicon consumption at first goes up (at a specific silicon consumption not more than 0.3 kg/kg $\text{V}_2\text{O}_5$) and then decreases. CO$_2$ mass does not exceed 0.00003 kg, O$_2$ mass does not exceed 0.03 kg with the reducing agents mass is zero, further in the gas phase it is present in the form of tracks.

Figure 1. Dependences of vanadium oxides mass on the temperature and reducing agents consumption (a – carbon consumption 0.05 kg/kg $\text{V}_2\text{O}_5$; b – carbon consumption 0.15 kg/kg $\text{V}_2\text{O}_5$; c – carbon consumption 0.25 kg/kg $\text{V}_2\text{O}_5$; g – carbon consumption 0.35 kg/kg $\text{V}_2\text{O}_5$).
Figure 2. Mass dependences of the condensed and gas phases on the reducing agents consumption in the system $V_2O_5$–C–Si system at 1873K (a – condensed phase; b – gas phase).
Figure 3. Mass dependences of the gas phase components on the consumption of reducing agents in the system $V_2O_5-C-Si$ at 1873K (a – mass of CO, kg; b – mass of SiO, kg).
From the data obtained it can be concluded that in the system V$_2$O$_5$–C–Si system the direct reduction of vanadium pentoxide with carbon takes place. In addition, carbon reduces the formed silica.

The calculation results of reduction products masses for the system V$_2$O$_5$–C–Si given in Figures 4, 5 and 6, showed that vanadium, reduced from the vanadium pentoxide during carbon-silicon thermal reduction, is mainly found in the form of vanadium carbide and vanadium silicides.

The results of thermodynamic calculations of the vanadium coreduction with carbon and silicon for the system V$_2$O$_5$–C–Si shows that vanadium reduction from vanadium pentoxide is initially occurs with formation of vanadium carbide (Figure 4), and further as the silicon consumption increases more than 0.3 kg/kg V$_2$O$_5$, vanadium silicides VSi$_2$, V$_5$Si$_3$ and V$_3$Si (Figure 5) are also formed.

The mass of the metallic vanadium according to the calculated data is insignificant and does not exceed 8% of the reduced vanadium mass. With the increase in the specific consumption of silicon this value decreases due to the formation of vanadium silicides (Figure 6).

Thermodynamic modeling showed that carbon is a predominant reducing agent during carbon-silicon thermal reduction of vanadium from pentoxide vanadium.

![Figure 4](image-url)

**Figure 4.** Mass dependences of vanadium carbide on reducing agents consumption in the system V$_2$O$_5$–C–Si at 1873 K.
The performed thermodynamic calculations showed that in the examined system the reduction products contain silicon carbide formed from SiO$_2$ in the reaction: SiO$_2$ + 3C = SiC + 2CO.
According to the dependency given in Figure 7 the amount of silicon carbide increases linearly with the increase in the amounts of the introduced reducing agents.

![Figure 7. Mass dependences of silicon carbide on the consumption of reducing agents in the system $V_2O_5$–C–Si system at 1873 K.](image)

3. Conclusions
The performed thermodynamic calculations of vanadium reduction from its oxides in the system $V_2O_5$ – C – Si demonstrated:
- at a temperature from 1673 to 2073 K this process depends only on reducing agents consumption. The temperature variation does not have any influence.
- vanadium reduction from vanadium pentoxide in combination with carbon and silicon takes place with predominant formation of vanadium compounds: vanadium carbide and vanadium silicides. Mass of metallic vanadium is not significant.

These results confirm the previous findings [8-10], and suggest that in the carbon-silicon thermal reduction vanadium carbon plays the basic role.

4. References
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