Thermodynamic modeling of restoring items converter vanadium slag

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Abstract. Calculations of parameters for equilibrium processes of iron, manganese, vanadium and titanium reduction from converter vanadium slag by carbon from small-sized coke and silica from ferrosilicon were performed by the method of thermodynamic modeling using the program complex “Terra”. Calculations were made for each type of reductant separately and in combination. Dependences of process parameters on reducing agents consumption were drawn. The analysis of the results was carried out.

1. Introduction
One of the most effective and demanded alloying elements for production of steels with high performance properties is vanadium, and the perspective technology of steel alloying is processing by converter vanadium slag using carbon and silicon as reducing agents [1-3]. However, industrial converter vanadium slags alongside with vanadium oxides (from 10 to 30% V₂O₅) contain iron, titanium, manganese, silicon and calcium oxides (10 ÷ 30 % SiO₂, 1 ÷ 5 % CaO, 1 ÷ 5 % MgO, 4 ÷ 12 % MnO, 25 ÷ 35 % Fe₂O₃, 2 ÷ 12 % TiO₂, 1 ÷ 3% Al₂O₃). Study of the recovery of elements in such complex multi-component oxide system is possible only with the use of modern methods and software products for thermodynamic modeling [4-7].

2. Research and results
Solving the problem of processes research of elements recovery from converter vanadium slag we used one of the methods for thermodynamic modeling based on the calculation of equilibrium parameters in the model of thermodynamic systems [8-10]. The advantage of these methods consists in the feasibility of multivariate calculations of equilibrium of multicomponent systems during varying in the wide range of control actions. Calculation of thermodynamic equilibrium can reveal the possibility of obtaining substances, the allocation of which is essential in addressing the task of evaluating limit end state, and determine the scope of the valid parameter values. When performing thermodynamic modeling the software product – program complex “Terra” was used, developed at Moscow State Technical University, which allows the equilibrium composition of multi-component
heterogeneous thermodynamic system for high temperature conditions to be found on the basis of the principle of maximum entropy [5].

While performing study of elements recovery from converter vanadium slag (16.0% V$_2$O$_5$, 5.0% TiO$_2$, 10% MnO, 25.0% Fe$_{tot}$) we made calculations of equilibrium compositions of heterogeneous mixtures of slag and reducing agents at a temperature of 1873 K. The boundary conditions were defined according to the calculations of vanadium extraction ratio $\eta_V$ for small-sized coke consumption in the range from 0 to 0.5 kg/kg of slag and ferrosilicon FeSi75 from 0 to 0.5 kg/kg of slag [11-12]. Vanadium extraction ratio $\eta_V$ is close to 1 at a specific consumption of small-sized coke more than 0.2 kg/kg of slag and ferrosilicon over 0.25 kg/kg of slag, these consumptions were chosen as boundary values.

Analysis of the calculations results presented in Figures 1 and 2 showed that the recovery of iron from iron oxides ends at a specific consumption of small-sized coke 0.1 kg/kg of slag, and restoration of silicon from ferrosilicon – 0.14 kg/kg of slag. Vanadium recovery begins after full iron recovery. The content of manganese oxides and titanium as the consumption of reducing agents increases varies slightly, indicating the limit of their recovery degree at a given temperature. During vanadium and titanium recovery by small-sized coke smaller values of residue content of their oxides in the recovery products in comparison with the ferrosilicon recovery (0.25 % and 1.3 % for vanadium, 0.08 % and 0.60 % for titanium respectively).

According to the estimated data presented in Figures 3-6, during carbon silicothermal recovery (by carbon from small-sized coke and silicon from ferrosilicon) the content of iron oxides in the recovery products of converter vanadium slag at a specific consumption of small-sized coke more than 0.1 kg does not depend on the consumption of FeSi75. Content of vanadium oxides decreases as the reducing agents (at any proportion) consumption increases and reaches 0.04 % at a specific consumption of small-sized coke more than 0.14 kg/kg of slag and ferrosilicon more than 0.2 kg/kg of slag. Content of titanium oxides in the slag less than 2 % is achieved at the specific consumption of FeSi75 more than 0.1 kg/kg of slag at any consumption rate of small-sized coke. The minimum number of titanium oxides is approximately 0.01 % at maximum consumptions of both reducing agents. Content of manganese oxide in the recovery products of converter vanadium slag is reduced via reduction by small-sized coke only or by ferrosilicon up to 1%.

During joint reduction of manganese from its monoxide by carbon from small-sized coke and silicon from ferrosilicon in the specified range of reducing agents consumptions we can achieve the content of oxide in the slag 0.5 % (Figure 6). It should be noted that the content of vanadium oxides at such reducing agents consumptions is less than 0.05 %. Manganese recovery is limited under these conditions.

![Figure 1. Dependence of the content of iron, vanadium, manganese and titanium oxides in slag on quantity of small-sized coke at 1873K (1 – iron oxides, 2 – vanadium oxides, 3 – manganese oxide, 4 – titanium oxides).](image)
Figure 2. Dependence of the content of iron, vanadium, manganese, and titanium oxides in slag on quantity of ferrosilicon at 1873K (1 – iron oxides, 2 – vanadium oxides, 3 – manganese oxide, 4 – titanium oxides).

Figure 3. Change in the content of vanadium oxides in the slag during joint reduction by carbon from small-sized coke and silicon from ferrosilicon.
Figure 4. Change in the content of iron oxides in the slag during joint reduction by carbon from small-sized coke and silicon from ferrosilicon.

Figure 5. Change in the content of titanium oxides in the slag during joint reduction by carbon from small-sized coke and silicon from ferrosilicon.
3. Conclusions
The results of the calculations of the content of vanadium carbide and metal vanadium in recovery products during joint reduction of converter vanadium slag by carbon from small-sized coke and silicon from ferrosilicon showed that vanadium recovery takes place with the formation of vanadium carbide. At a given quantity of reducing agents (up to 0.2 kg of small-sized coke and 0.25 kg of ferrosilicon) iron and vanadium from converter vanadium slag are almost completely recovered [11-12]. Titanium in recovery products of converter vanadium slag according to estimated data are also in the form of titanium carbide. When the quantity of reducing agents consumption is less 0.20 kg per 1 kg of converter vanadium slag full recovery of titanium and manganese from their oxides does not occur even at maximum consumptions of both reducing agents [11-12].

The results of thermodynamic calculations proves that at given specific consumptions of reducing agents the carbon silicothermal recovery of vanadium and iron from converter vanadium slag by carbon and silicon proceeds quite successfully alongside with the limited recovery of titanium and manganese.

4. References
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