Conference Paper

Thermodynamic Modeling of Iron and Nickel Reduction from B_2O_3-CaO-FeO-NiO Melts

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Abstract

At present, during solving theoretical and applied problems of metallurgical technologies improving, thermodynamic modeling (TDM) methods are widely used to calculate multicomponent and multiphase systems. However, existing methodology ТДМ are intended for the balance analysis in the "closed" systems. The authors of [9] proposed a technique that allows, using TDMs, to describe metal reduction processes during gas bubbling of multicomponent oxide melts in approximation to "open" real systems. The applicability of the methods is estimated using the example of joint Nickel and Iron reduction modeling in the B_2O_3-CaO-FeO-NiO system by Carbon monoxide for "open" and "closed" systems. The data obtained comparison for "open" and "closed" systems show that the consecutive output of products (gas and metal) from working medium promotes achievement of the best parameters for Nickel extraction to alloy and to its residual content in oxide melt. Using this technique, the ТДМ process of joint reduction of Nickel and Iron in system B_2O_3-CaO-FeO-NiO by Carbon monoxide in "open" system was undertaken at various temperatures in the 1273-1773K interval.

Keywords: thermodynamic modeling, "closed" system, "open" system, joint reduction, Carbon monoxide, oxide melt, gas bubbling.

The widespread use of methods for the metals reduction from oxide melts [1–7] is explained by the possibility of its selective selection by varying the quantity of injected gas (CO, H_2, CH_4, conversion products). In the research majority, real productions slags were used as starting materials, having different forms of metal compounds, including oxide-sulfide solution and mechanically removed matte. Due to the slag structure complexity, conclusions about mechanism and kinetics of metal reduction are not always justified.

As an applying aspect, the research of metal reduction mechanism is impotent for bubble processes development. Such processes are widely used in the metallurgy of ferrous and non-ferrous metals. For example is smelting of oxidized Nickel ores in Vanyukov furnace. Bubbling of oxide melt (slag) is carried out with natural gas in a number of processes [3, 4]. Such injection into the high temperature range leads to thermolysis and formation of Hydrogen and Carbon, which are redacting agents.

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Irregular distribution of carbon in the oxide melt volume leads to the intensive Iron reduction, which, due to its higher density, transits into the bottom phase. The reverse transition of Iron to oxide melt during interaction with non-ferrous metal oxides is delayed by diffusion. Therefore, the bottom phase (Fe – Ni alloy), can only conditionally be considered as equilibrium phase in the system under researching. The works [5, 6] related to the research of the Oxygen potential of gases influence to the reduction process showed that at Carbon absence, the Iron content in the metal can be controlled and, thereby, the Nickel content can be increased in ferronickel.

At present, during solving theoretical and applied problems of metallurgical technologies improving, thermodynamic modeling (TDM) methods are widely used to calculate multicomponent and multiphase systems. Modeling determines the equilibrium values, thermodynamic properties, chemical and phase compositions. Such parameters are necessary for analysis of the melts reduction processing and extraction of non-ferrous metals from slag. The calculation results provide data on the non-ferrous metals forms, its distribution between alloy and slag, as well as the effect of the gas phase Oxygen potential to the systems properties [7, 8].

However, the existing TDM methodologies [7, 8] are intended for the analysis of equilibrium in "closed" systems. As applied to the description of the reduction of metals from an oxide melt, this is as follows. The amount of reducing agent is set by its simultaneous introduction into the composition of the working body with an unchanged number of other components.

The authors of [9] proposed a technique that allows using TDMs to describe metal reduction processes during gas bubbling of multicomponent oxide melts in approximation to "open" real systems. The calculation is divided into cycles, in each subsequent of which only the oxide phase is provided with the achieved content of oxides of the metals being reduced and the gas and metal component are removed from the system. The calculation is carried out according to (Z) sequential cycles with the introduction of a reducing agent in the number of (n) moles in a single portion.

The applicability of the methods is considered on the example of modeling the process of joint reduction of nickel and iron in the B_2O_3-CaO-FeO-NiO system with carbon monoxide at a temperature of 1473 K and a pressure of 0.1 MPa. The initial composition of the melt, mol: B_2O_3 - 25.58, CaO - 10.83, FeO - 8.64, NiO - 0.83. The equilibrium calculations in the "closed" and "open" systems are carried out under the condition that the oxide and metal phases are ideal solutions.

Figure 1 shows the effect of the total amount of introduced CO on the compositions of the oxide, metal, and gas phases in the system under consideration. As follows from the data obtained, in the initial melt (without CO additives), FeO is disproportionate to

Fe and Fe_3O_4, and the exchange reaction between Iron and Nickel oxide leads to the formation of an alloy containing 92% Ni. CO additives lead to a monotonic decrease in the contents of NiO and Fe_3O_4 in the oxide melt, while the proportion of FeO initially increases to 20%, and only then decreases. The proportion of Iron in the form of metal increases in proportion to the amount of reducing agent introduced. The fraction of reduced Nickel reaches 100% already with the introduction of CO in an amount of 36 dm^3/kg of oxide melt.

Obtained data Comparison for the "open" and "closed" systems shows that the sequential removal of products (gas and metal) from the working body contributes to achieving better indicators for the extraction of Nickel in the alloy and its residual content in the oxide melt.
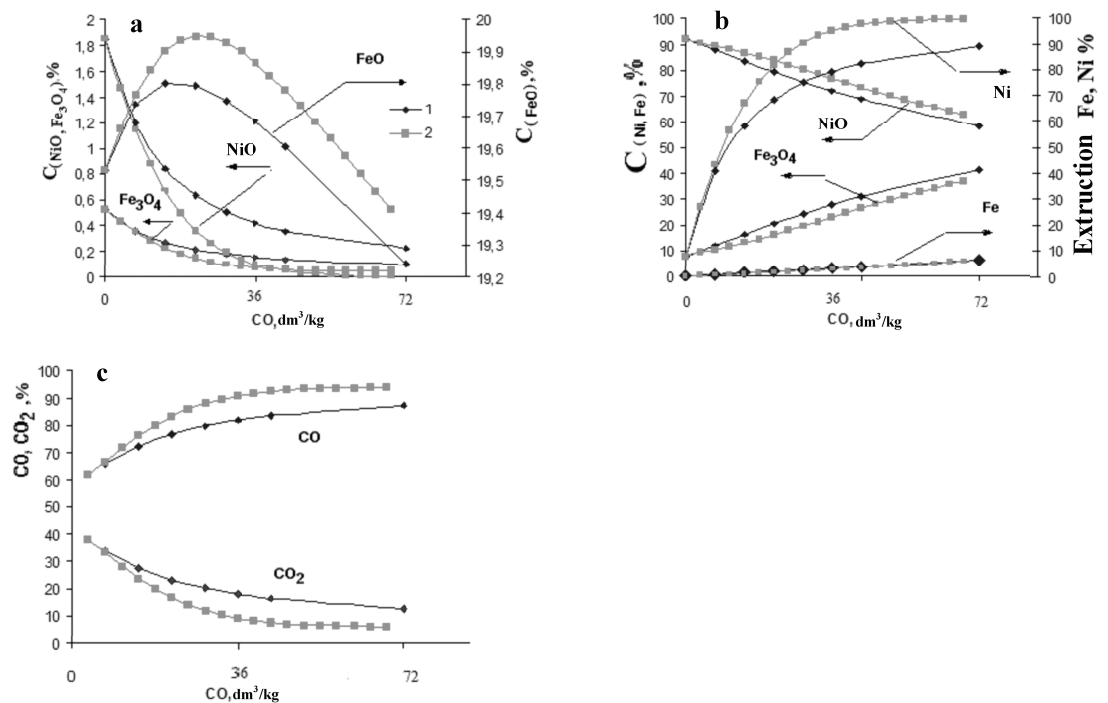

Figure 1: Contents change of the reduced oxides in the melt (a), metal (b) and gas phases (c) in the simulating process for the "closed" (1) and "open" (2) systems

Previously, using the developed TDM methodology in approximation to "open" systems [9], an analysis of the Hydrogen reduction of Iron and Nickel from a multicomponent oxide melt of the B_2O_3-CaO-FeO-NiO system was performed [10]. The calculations were carried out in the temperature range 1473-1823 K at a pressure of 0.1 MPa and a single portion of Hydrogen 0.1 mol. The content of Nickel oxide in the melt is reduced to 0.04 wt.%. In this work, we present the results of calculations by the proposed method for

the reduction of metals in the B_2O_3-CaO-FeO-NiO system with Carbon monoxide (in a single portion of 0.5 mol) in the temperature range 1273-1773 K.

As expected, the temperature affects the disproportionation of FeO: the amount of Fe_3O_4 at 1273 K is significantly higher than at 1773 K. The proportion of metallic Iron and Nickel increases symbatically:

$$4FeO \rightleftarrows Fe_3O_4 + Fe \text{ MeT,} \tag{1}$$

$$Fe_{MeT} + NiO \rightleftarrows Ni_{MeT} + FeO. \tag{2}$$
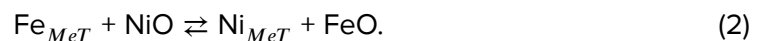
In the considered system, the content of metallic Iron decreases in temperature range (1273-1773 K) from 0.006 to 0.002 mol and Nickel from 0.064 to 0.019 mol. These values, although they make up small percent of the initial metals content in the oxide system, it indicate that the metal is formed due to exchange reactions (Fig. 2) even without gaseous reducing agent injection.
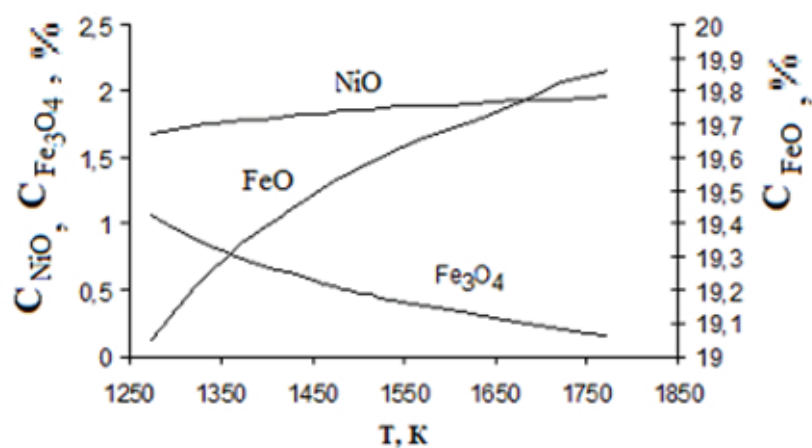

Figure 2: Oxide melt content temperature dependence.

During the reduction process (Fig. 3), the content of Nickel oxide in the melt decreases monotonically, and Iron oxide behaves similarly to the previous model experiment. An increase in the amount of CO introduced leads to increase of the metallic Iron and Nickel proportion. Initially, Nickel reduction proceeds preferably. After the main Nickel mass is reduced, the transition of FeO to Fe_{met} becomes noticeable, which leads to decrease of the FeO and Fe_3O_4 concentration in the melt. In the temperature range considered, the following phase transformations occur: $Ni_{solid} \rightarrow Ni_{liquid}$ (1725 K), $FeO_{solid} \rightarrow FeO_{liquid}$ (1651 K), $Fe_{solid} \rightarrow Fe_{liquid}$ (1812 K), which is reflected in the reaction equilibrium constants. A decrease in the equilibrium constants on temperature changes reduction degree of the corresponding oxide, which leads to increase in its residual content in the melt.

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increase in the amount of CO introduced leads to an increase in the proportion of metallic Iron and Nickel. Initially, Nickel reduction preferably proceeds. After the bulk of nickel is reduced, the transition of FeO to Fe_{met} becomes noticeable, which leads to a decrease in the concentration of FeO and Fe_3O_4 in the melt. In the temperature range under consideration, phase transformations occur: $Ni_{solid} \rightarrow Ni_{liquid}$ (1725 K), $FeO_{solid} \rightarrow FeO_{liquid}$ (1651 K), $Fe_{solid} \rightarrow Fe_{liquid}$ (1812 K), which is reflected in the reaction equilibrium constants. A decrease in the equilibrium constants with temperature changes the degree of reduction of the corresponding oxide, which leads to an increase in its residual content in the melt.

The compositions of the oxide and metal phases change depending on temperature (Fig. 4). Several intervals can be distinguished, with boundaries corresponding to the temperatures of polymorphic transformations. Up to 1651 K, at temperature increase, the equilibrium constant of the Nickel reduction reaction decreases, while Iron increases. This process affects composition of the formed ferronickel. In the ranges of 1651-1725 K, 1725-1812 K and above 1812 K, both constants decrease at temperature increasing. Its ratio is such that, depending on temperature, the Nickel content in ferronickel first decreases, and then begins to grow. Interest is to evaluate the technology parameters, such as the reducing gas consumption and its utilization coefficient. The more temperature increase, the longer process time is required to achieve equal performance. The gas utilization rate decreases at temperature increase. The equilibrium constants of metal reduction reaction by Hydrogen [10] are larger than Carbon monoxide (this work).
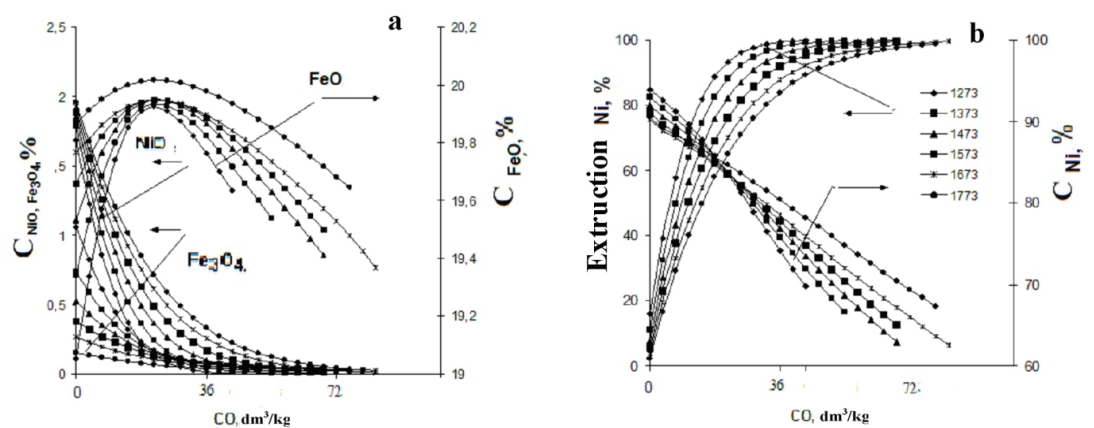

Figure 3: Effect of reducing agent (CO) injected to the contents of NiO, FeO, Fe_3O_4 in the oxide melt (a), Nickel in the alloy and its extraction into metal (b).
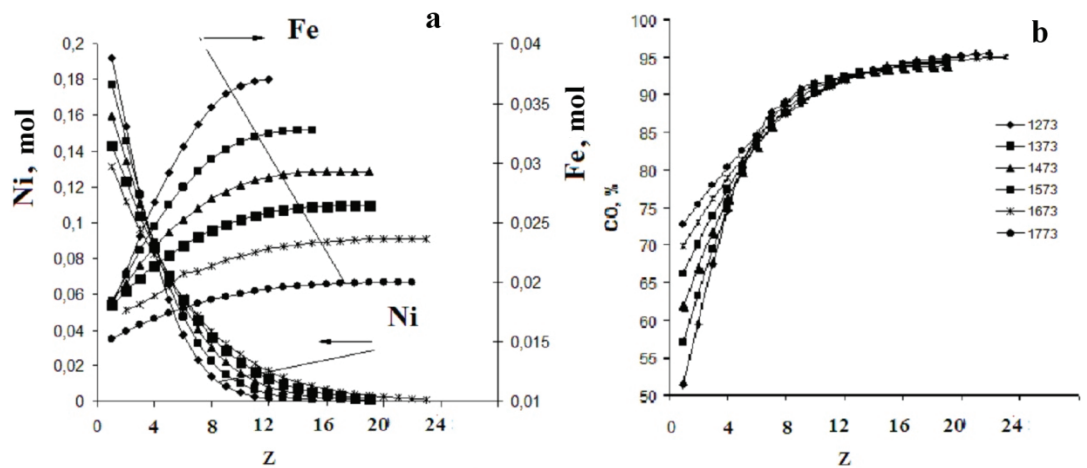
Figure 4: Change of Nickel and Iron quantity reduced by single portion of Carbon monoxide (a) and equilibrium CO content in the gas (b)

1. Conclusion

The calculation results of equilibrium in the B_2O_3-CaO-FeO-NiO system for the "open" and "closed" systems approximation are some different. The initial alloy formation with high Nickel content is associated with disproportionation of Iron oxide. The removal of reaction products from the working body promotes reduction of Nickel, which ensures its extraction completeness from oxide melt. Qualitatively, the process of metals reduction considered from the B_2O_3-CaO-FeO-NiO melt by Hydrogen and CO goes by the same way. For the same metal quantity reduction, Hydrogen consumption is considerably less than Carbon monoxide, because the equilibrium constants of reactions for Hydrogen are several times higher than for CO.

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