Thermodynamic modeling of the Mn and Cr reduction from slag

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Abstract: The complete thermodynamic modeling method and the TERRA package were used to calculate the elements distribution between metal, slag and gas during ferromanganese and ferrosilicochrom melting

Key words: Metallurgy, Thermodynamic Modeling, Slag, Reduction

1. Introduction

Metallurgical melts, such as Mn and Si containing metal and slag, is a solutions with strong chemical interaction between components. Therefore, there are difficulties with an adequate description of the thermodynamic activities of components and the calculated correctly modeling of the distribution of elements between metal and slag. In this paper demonstrates how the model of associated solutions and TERRA package [1] help solve these problems.

2. Experimental

2.1 Basic of calculation method

The composition of liquid solutions was described using the associated solution model. Liquid metal components were taken to be the Cr, Mn, Fe, Si, CrSi, Cr_5Si_3, $CrSi_2$, $CrSi_3$, Mn_3Si, Mn_5Si_3, MnSi, $MnSi_{1,7}$, Fe_3Si, Fe_5Si_3, FeSi, $FeSi_2$, Fe_3C, $Mn_{23}C_6$, Mn_3C, Mn_7C_3, groups (clusters), whose compositions were identical to those of the compounds that actually existed in the Fe–Si, Mn–Si, Cr–Si, Fe–C and Mn–C systems. Liquid slag components were taken to be the FeO, MnO, MgO, CaO, SiO_2, Al_2O_3, Cr_2O_3, Cr_2SiO_4, Fe_2SiO_4, $MnSiO_3$, Mn_2SiO_4, Al_2SiO_5, $CaSiO_3$, Ca_2SiO_4, $MgSiO_3$, Mg_2SiO_4, $FeCr_2O_4$, $MgCr_2O_4$, $CaCr_2O_4$, $MgFe_2O_4$, $MgAl_2O_4$, $FeAl_2O_4$. The thermodynamic properties of the groups in liquid solutions were described by the thermodynamic properties of the corresponding compounds at the temperatures of the solutions. In the associated solution model (the approximation of ideal solutions of interaction products), the heats of mixing of groups are assumed to be zero, and the entropy of mixing is calculated as for ideal solutions. The solutions composition is determined by the equilibrium state of the whole metal–slag–gas system when the system reaches a global thermodynamic potential extremum (entropy maximum) in the transformed isolated system.

2.2 Thermochemical data sources

Special attention was paid to verification, approval and adjustment of thermochemical data of individual substances. Comparison of the calculated (in accordance with the model of associated solutions) and experimental thermodynamic characteristics of solutions was the basis of test. For example, a comparison of calculated and experimental data for metallic melts Mn-Si and Cr-Si is shown in Fig. 1–4; for activities of oxides in certain slag systems – is shown in Fig. 5–7. The calculations of the distribution of elements between metal and slag was carried out after adjusting the thermodynamic data.

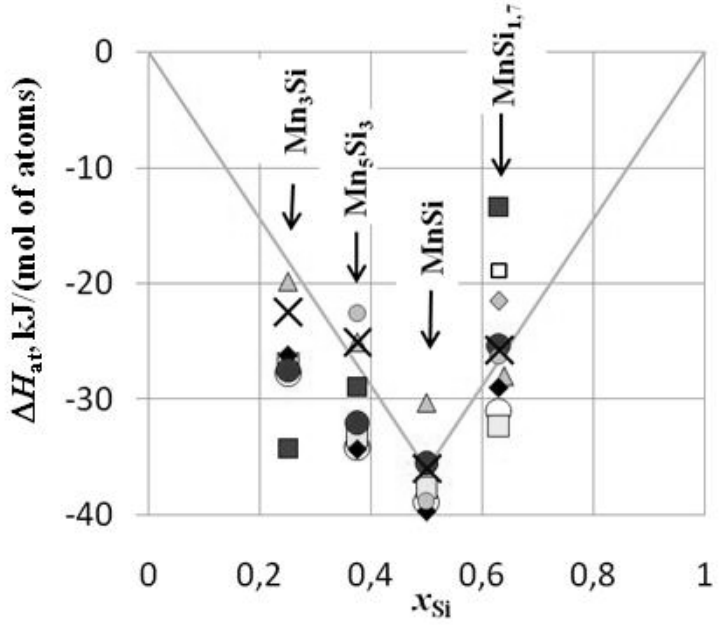

Fig. 1. The manganese silicides heat of formation; X – accepted in this work; other dots – data of other authors

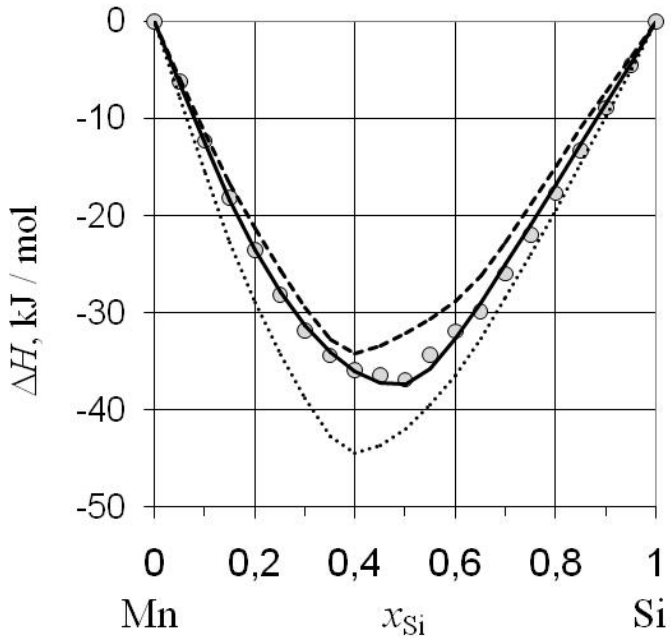

Fig. 2. Heat of mixing in Mn-Si solutions at 1773 K: dots – the experimental data of Geld, 1974; solid line – this work; dot lines – calculated data of other authors

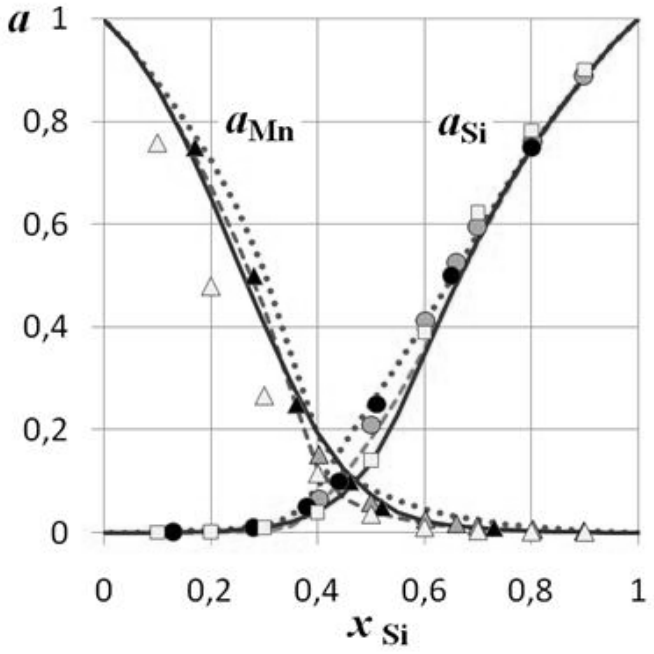

Fig. 3. Activities of elements in Mn-Si solutions at 1773 K; solid line – this work; dots and dot lines – experimental and calculated data of other authors

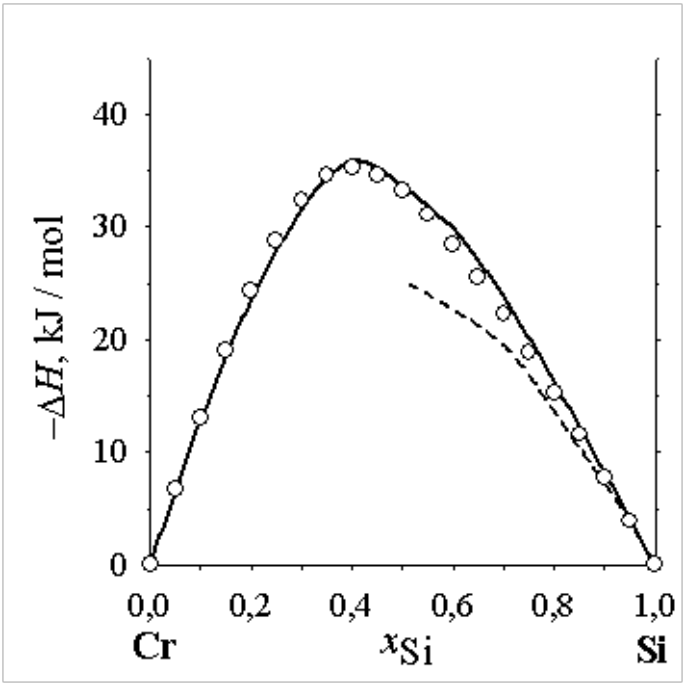

Fig. 4. Heat of mixing in Cr-Si solutions at 2000 K: dots – the experimental data of Geld, 1976; solid line – this work

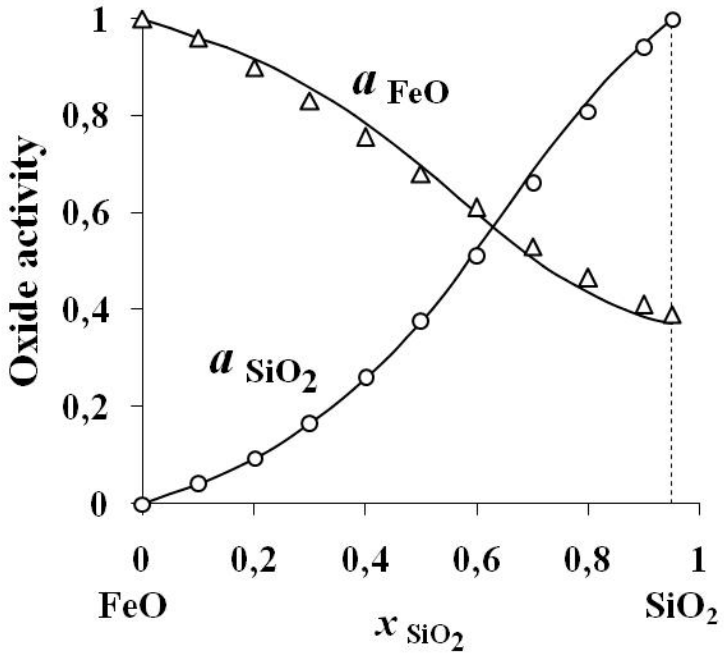

Fig. 5. Activities of simple oxides in the FeO–SiO_2 system at 1873 K; lines – experimental data; dots – calculated in this work

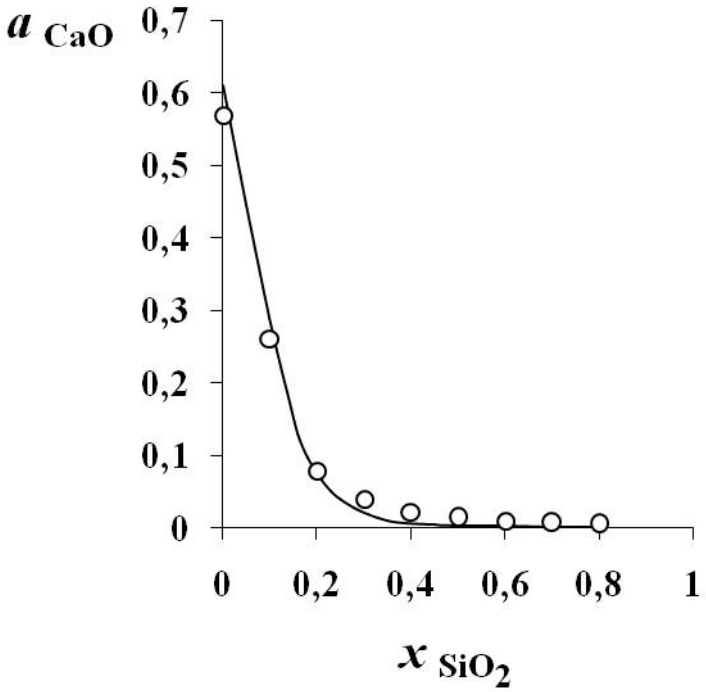

Fig. 6. Activity of CaO in the Al_2O_3–CaO–SiO_2 system at 1873 K along the section 60 wt % Al_2O_3, 40 wt % CaO – 90 wt % SiO_2 and 10 wt % CaO; lines – experimental data; dots – calculated in this work

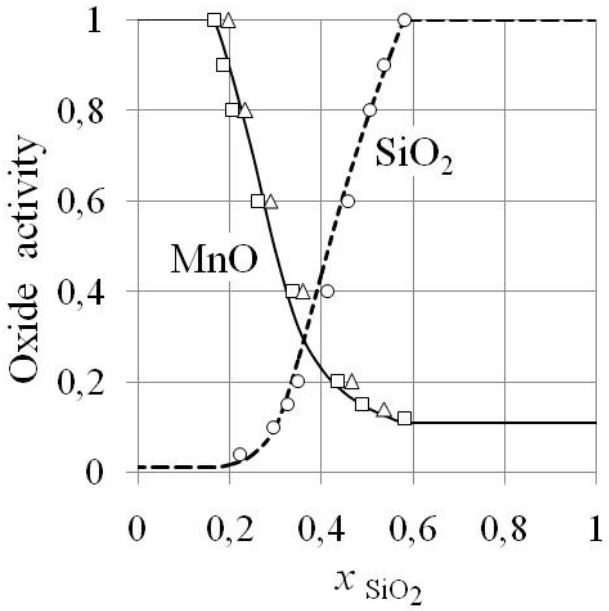

Fig. 7. Activities of simple oxides in MnO-SiO_2 solutions at 1873 K; dots – the experimental data; lines – calculated in this work

Modeling was performed for the Mn–Si–Fe–Al–Ca–Mg–O–C and Cr–Si–Fe–Al–Ca–Mg–O systems. The initial complete thermodynamic modeling parameters were the overall system composition (a fixed amount of the ore and variable amount of the reducing agent), total pressure 0,1 MPa (1 atm), and the temperature of the equilibrium state. The primary complete thermodynamic modeling information was used to calculate the elements distribution.

3. Results

Calculation information about changing the composition of the metal, slag and other indicators of reduction of chromium ore slag by ferrosilicium is shown in Fig. 8 (ore composition, wt. %: 41,94 Cr_2O_3; 9,55 FeO; 3,3 Fe_2O_3; 7,58 Al_2O_3; 23,55 MgO; 10,26 SiO_2; 3,44 volatile components; 1,000 kg of ore added 100 kg CaO). Information about changing the composition of the metal at reduction the model slag MnO-SiO_2 (MnO/SiO_2 = 60 wt/% / 30 wt/%) is shown in Fig. 9. Samples of slag and metal after reduction the manganese containing furnace dust are shown in Fig. 10 (laboratory experiment; reducing agent – ferrosilicium; 62 % the degree of Mn reduction).

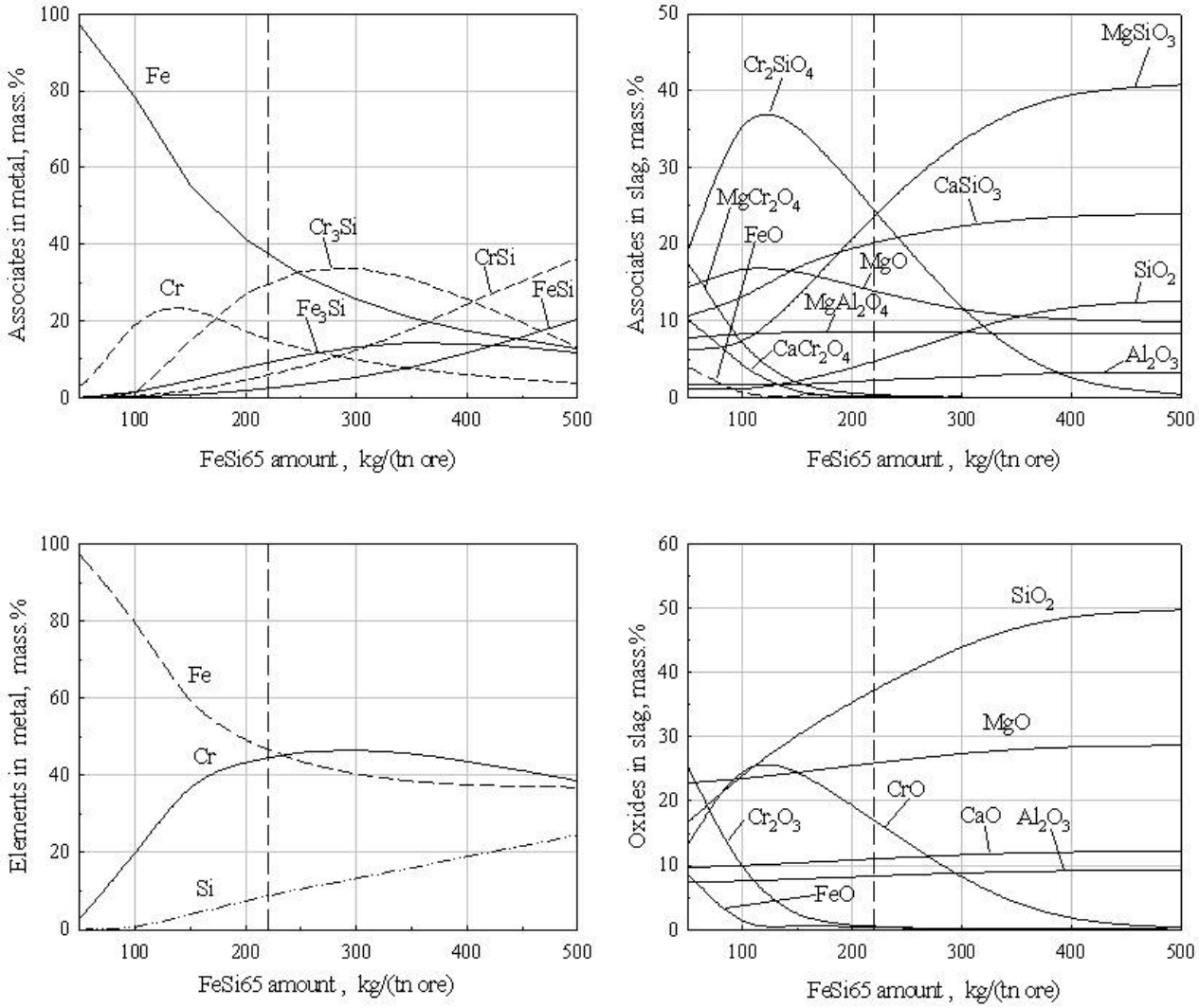

Fig. 8. Composition of metal and slag depending on amount of reducing agent at 1973 K (dashed vertical line is stoichiometric amount of reducing agent)

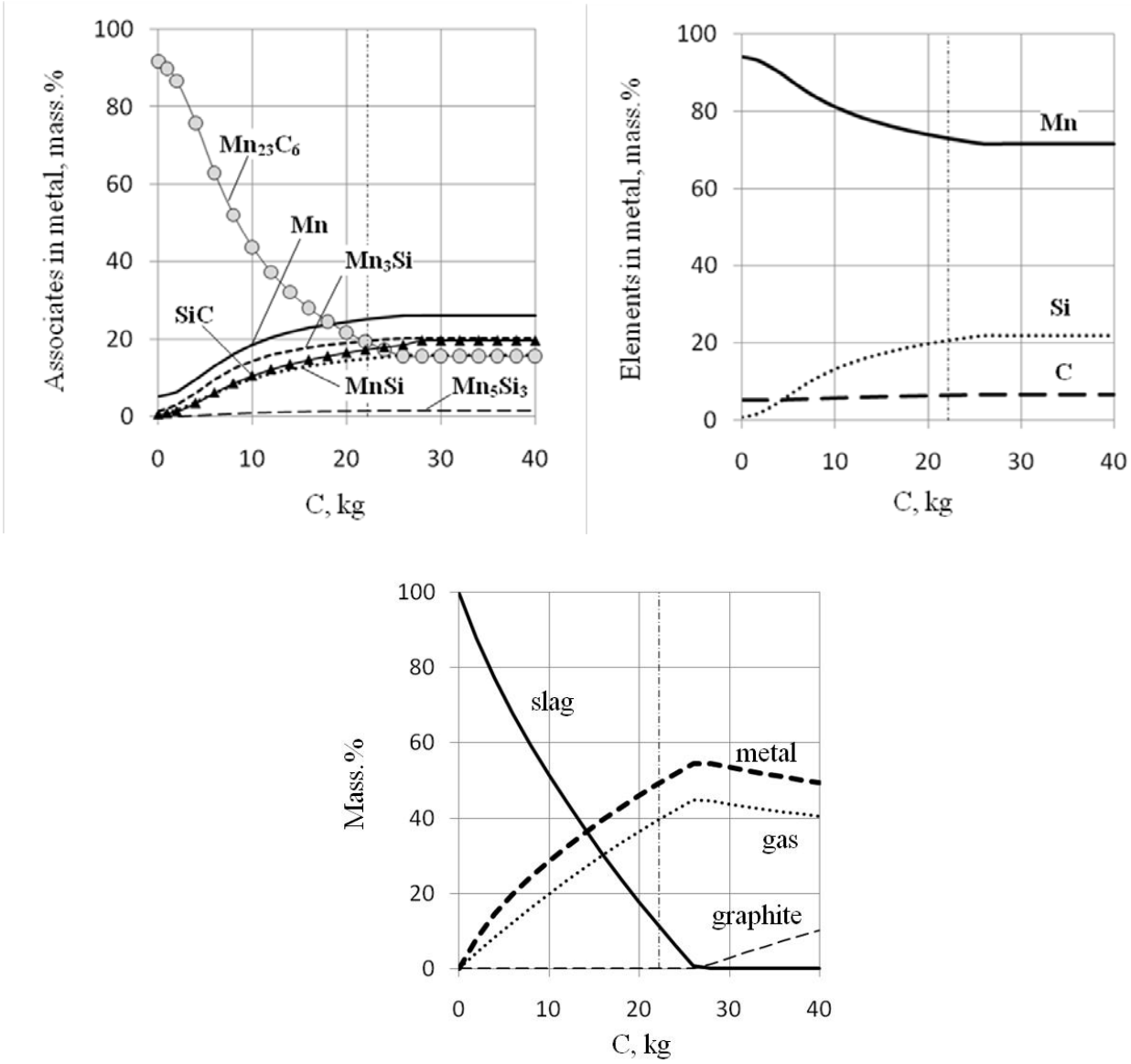

Fig. 9. The metal and the system composition depending on amount of reducing agent at 1773 K

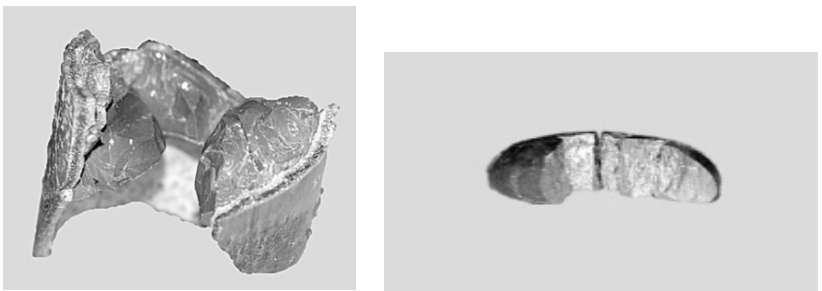

Fig. 10. The samples of reducing slag and MnFeSi-metal

4. Discussion

Difficulties of the Mn and Cr reduction are exist due to $MnSiO_3$, Mn_2SiO_4, and Cr_2SiO_4 clusters in slag. The calculation results correspond the literature experimental data.

5. Conclusions

It follows from the calculation results that the model of associated solutions and the thermodynamic characteristics of substances used give a correct description of the elements distribution in liquid metal and oxide solutions. The procedure that we used can be applied to describe high-temperature equilibria between metals and slags in thermodynamic modeling of metallurgical processes.

References

[1] N.A. Vatolin, G.K. Moiseev, B.G. Trusov. Thermodynamic modeling in high-temperature inorganic systems. Moscow, Metallurgy, 1994, 352 p, in Russian