Phase equilibriums in the “liquid metal – nonmetallic and intermetallic complex phases, including molten slags, fluxes and salts” systems

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Abstract: The system of the thermodynamic analysis of processes in the presence of liquid metal is elaborated. It allows sufficiently and thermodynamically adequately describe the processes which occur in processes of interaction of metal melts with complex composition and equilibrium complex phases (nonmetallic and intermetallic, including molten slags, fluxes and salts) which are in different state of matter. The created system is based on calculating coordinates of the surfaces of components solubility in metal melt (SCSM). These are special multicomponent phase diagram, which allows to adjust the microchanges in the metal alloy in accordance with the qualitative change in the composition of the complex phases. They allow to solve numerous problems connected with the development and optimization of various technological processes. Particularly it concerns the following problems: rational metal refining and evaluating complex alloys structures, determining the limits of technological additives refining effect and sequences of nonmetallic phases under temperature or metal structure changes. During this work SCSM of the systems on the basis of copper, cobalt, nickel, aluminum, lead, bismuth, tin and indium for a wide range of composition and temperatures is plotted. The results of calculating the surfaces of components solubility in metal melt have been compared with the data presented in relevant scientific papers and the results of own experiments, namely the X-ray microanalysis of nonmetallic and intermetallic inclusions formed in metal melts, with different contents of impurities in metal structure.

Key words: Thermodynamic calculations, Phase equilibria, Metal melt, Nonmetallic and intermetallic complex phases, Pyrometallurgical processes

1. Introduction

In metallurgy, technology of alloys and nanomaterials and in some other productions various heterogeneous processes take place in presence of the metal melts: oxidation, reduction, thermal decomposition of complex substances, gas-core interaction with following precipitation of the generated products etc. The method of thermodynamic modeling is very useful for organization of controlling of such processes. The approach which until recently was used for analysis of the heterogeneous processes in the metal melts with the nonferrous metals is based on consideration of the separate chemical reactions occurring in the analyzed system. This method does not allow to consider the mutual interaction of the complex chemical composition of the interacting phases on the nature of the generated product completely.

The system of the thermodynamic analysis of processes in the presence of liquid metal is elaborated. It allows sufficiently and thermodynamically adequately describe the processes which occur in processes of interaction of metal melts with complex composition and equilibrium complex phases (nonmetallic and intermetallic, including molten slags, fluxes and salts) which are in different state of matter. The created system is based on calculating coordinates of the surfaces of components solubility in metal melt (SCSM). These are special multicomponent phase diagram, which allows to adjust the microchanges in the metal alloy in accordance with the qualitative change in the composition of the complex phases [1]. They allow to solve numerous problems connected with the development and optimization of various technological processes. Particularly it concerns the following problems: rational metal refining and evaluating complex alloys structures, determining the limits of technological additives refining effect and sequences of nonmetallic phases under temperature or metal structure changes. During this work SCSM of the systems on the basis of copper, cobalt, nickel, aluminum, lead, bismuth, tin and indium for a wide range of composition and temperatures is plotted. The results of calculating the surfaces of components solubility in metal melt have been compared with the data presented in relevant scientific papers and the results of own experiments, namely the X-ray microanalysis of nonmetallic and intermetallic inclusions formed in metal melts, with different contents of impurities in metal structure.

Let’s review some of plotted SCSM.

2. SCSM of Ni–Al–O system

Line 1–2 in figure 1 shows compositions of the liquid metal, which is in equilibrium with solid NiO and solid spinel ($NiAl_2O_4$). The compositions of the metal, which is in equilibrium with solid NiO are, determined in area I. The compositions of the metal, which is in equilibrium with solid spinel, $NiAl_2O_4$ are determined in area II. The compositions of the liquid metal which is in equilibrium with solid spinel $NiAl_2O_4$ and solid NiO are shown on lines 3–4, and compositions of the liquid metal which is in balance with solid Al_2O_3 are determined in area III.

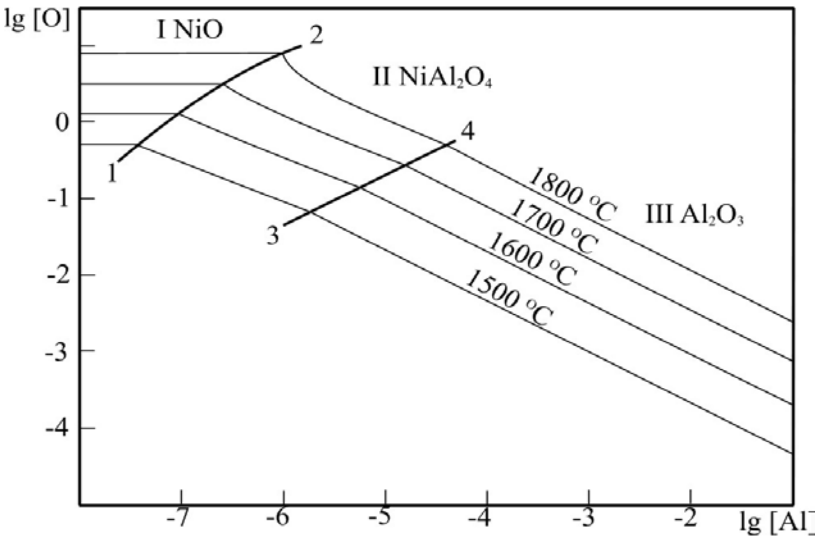

Fig. 1 SCSM of the Ni–Al–O system

3. SCSM of Pb–Cu–S system

The Pb–Cu–S system is of interest from the point of view of analysis copper removal from the lead during which copper extracts as Cu_2S as a result sulfur (or lead sulphide concentrate) addition to the lead melt.

The SCSM of the system is shown in figure 2. There we can see how the composition of the condensed elements balanced with the lead melt changed against the content of copper and sulfur in the liquid metal.

Concentrations of the components (mas %) in logarithmic scale are reproduced on the coordinate axis. Boundaries of the areas of the phase equilibrium of the metal with solid phases are shown with contrast lines. Solubility isotherms of sulfur and copper under their mutual existence in liquid lead are shown with thin lines. In area I (with low content of sulfur in the system) the phase balanced with the lead melt is solid pure copper, in area II the melt is joined with copper sulphide (Cu_2S) and in area III with solid lead sulphide (PbS).

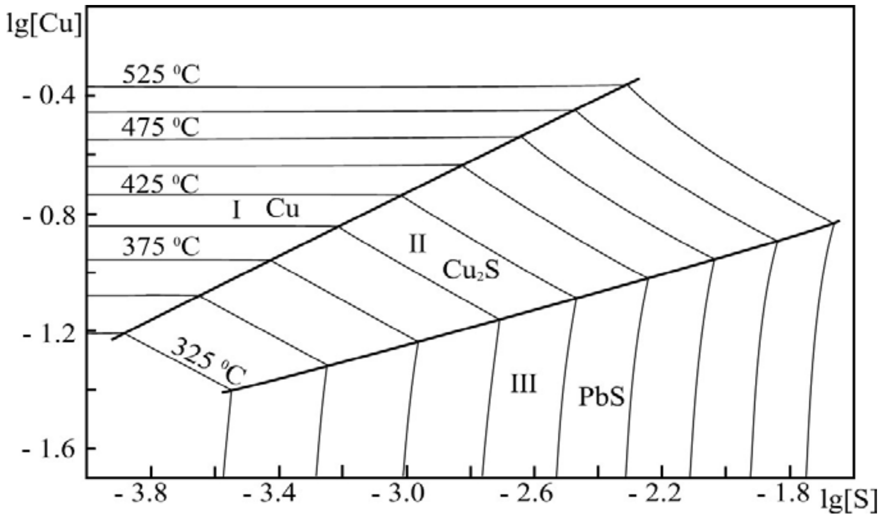

Fig. 2 SCSM of the Pb–Cu–S system

4. SCSM of Al–Mg–O system

With the help of the SCSM of the Al–Mg–O system shown in figure 3 we can see how the composition of the oxidation products of the alumi-magnesium melt changes depending on the content of magnesium in the liquid metal.

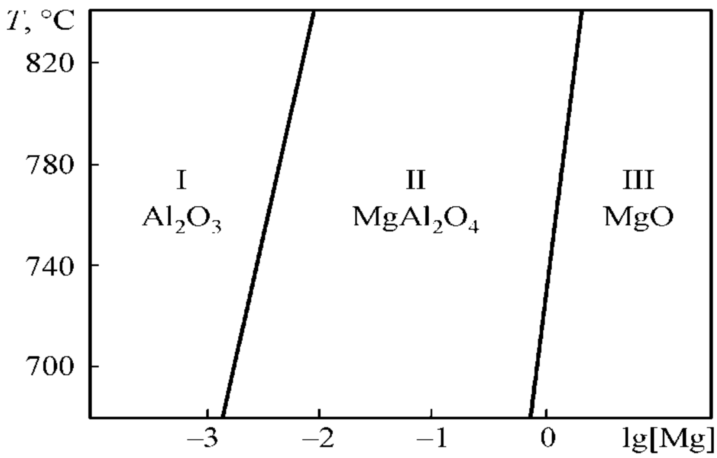

Fig. 3 SCSM of the Al–Mg–O system

Content of magnesium in the logarithmic scale is reproduced on the abscissa axis. In area I the solid Al2O3 is generated as a result of the reaction between the melt metal and oxygen, in area II the crystal magnesium aluminate (MgAl2O4) is generated, and in area III the solid oxide of magnesium is generated (MgO).

5. SCSM of Co–C–O system

As an example of systems on the basis of cobalt we can analyze SCSM for the Co–C–O system plotted in the course of our work (figure 4). The calculation was done for two variants of the gas phases composition. In the first instance we took the total partial pressure of carbon dioxide and carbon monoxide gases as 0.1 atm. In the second instance it was 1 atm.

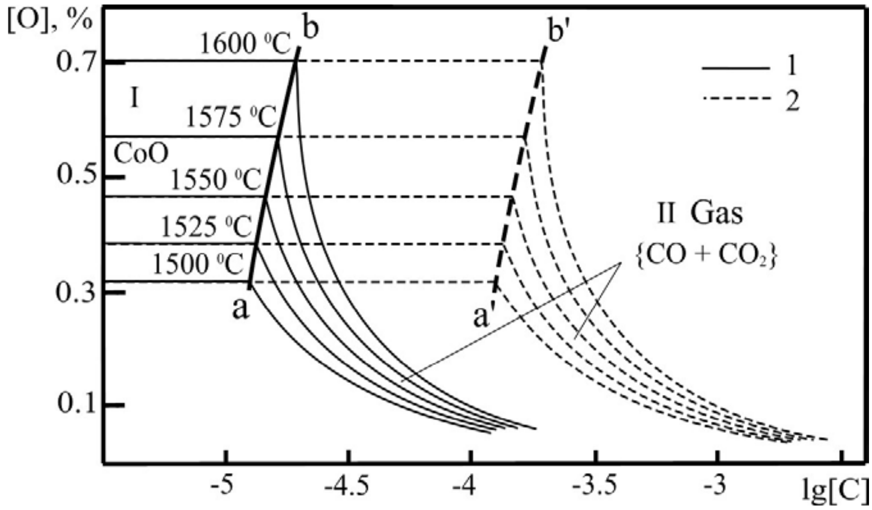

Fig. 4 SCSM of the Co–C–O system

1 – sum of partial pressures of carbon oxides 0.0101 MPa;

2 – sum of partial pressures of carbon oxides 0.1013 MPa.

In area I the phase balanced with the cobalt melt is solid CoO, in area II the melt is joined with the gas phase (CO, CO_2). The concentration of CO_2 is negligible. Line ab shows compositions of the liquid metal, which is in balance with solid CoO and gas phase. The increase in pressure of carbon oxides shifts the phase boundary ab in the direction of higher carbon concentrations in liquid metal (the line a'b').

6. SCSM of Bi–Ag–Zn system

The SCSM of the Bi–Ag–Zn system constructed in the course of performing calculations is shown in figure 5.

Contrast lines depict the areas of phase equilibria of metal with solid phases, thin lines depict the solubility isotherms of silver and zinc in the case of their joint presence in the liquid bismuth, and the numbers I–V denote the areas characterizing the compositions of metal in equilibrium:

I – with the silver-based solid solution;

II – with the nonstoichiometric solid phase AgZn;

III – with the solid intermetallic phase Ag_2Zn_3;

IV – with the nonstoichiometric solid phase $AgZn_{2.5–7}$ ($AgZn_5$) and

V – with the zinc-based solid solution.

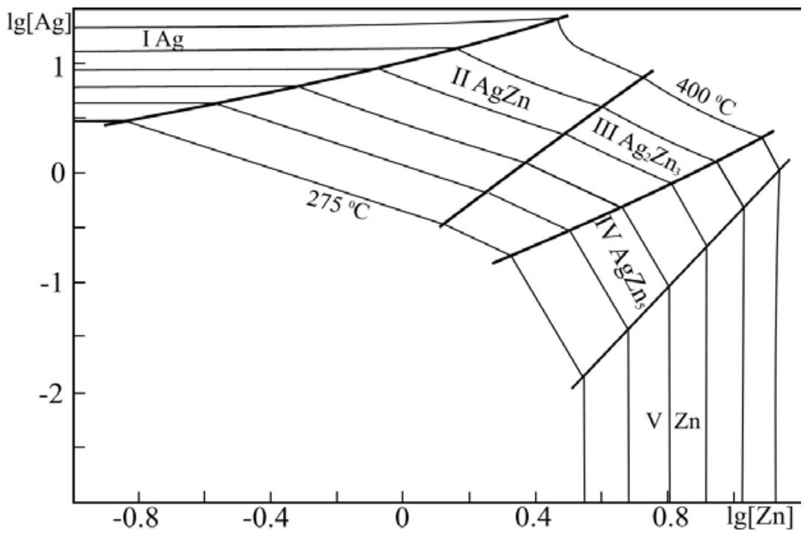

Fig. 5 SCSM of the Bi–Ag–Zn system

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