DECOMPOSITION of IRON, COBALT and NICKEL SELENIDES in SELENIUM DISTILLATION CONDITIONS

Abstract: Using diagrams of partial pressure the behavior of iron selenides, nickel and cobalt in a distillation process is investigated at temperatures of selenium boiling point of 672 °C at atmospheric pressure and 400-500 °C in vacuum. In the context of the distillation of selenium from its melts in vacuum at 400-530°C thermodynamically stable phase of the existence of iron impurities is diselenide \( \text{FeSe}_2 \) (crys.), the dissociation of the compound is not expected. At temperatures from 530 °C to 672 °C (the boiling temperature of selenium, we have found) and pressures of 0,013-6,46 kPa decomposition of iron diselenide into Fe monoselenide occurs with selenium transfer into the vapor phase. Decomposition of iron monoselenide in conditions of the selenium distillation from the melt is impossible. In the melt admixture of cobalt is in the form of stable phase of crystalline cobalt diselenide - \( \text{CoSe}_2 \) (cryst.). At temperatures above 607 °C in the pressure range 13-200 Pa it is possible dissociation \( \text{CoSe}_2 \) (cryst.) with formation of monoselenide \( \text{CoSe} \) (cryst.) and selenium vapor. Nickel in the selenium melts at atmospheric and low pressures is presented in the form of a stable phase – nickel monoselenide \( \text{NiSe} \), which is similar to the behavior of nickel sulphides in industrial processes. As a result, it is found that, in the conditions of vacuum and distillation selenium transfer into the vapor phase and at the presence of metal impurities in the melts, ferrous diselenide \( \text{FeSe}_2 \) (cryst.), cobalt diselenide \( \text{CoSe}_2 \) (cryst) and nickel monoselenide \( \text{NiSe} \) (cryst.) are thermodynamically stable. Increase of the process pressure to atmospheric pressure of 0.1 MPa does not change the composition and stability of the compounds.

Key words: selenium, iron, nickel, cobalt, monoselenides, diselenides, partial pressure diagram.

Introduction. The distillation process for treatment of selenium containing materials and for selenium refinement carried out in the process equipment made of alloy steel, is accompanied by formation of higher ferrous selenides [1] and (a priori) its alloying metals, i.e. nickel and cobalt included in the triad.

In this connection, the behavior of ferrous, nickelous and cobaltous selenides in the conditions of the distillation process implemented at temperatures of selenium boiling (672 °C, 945 K) at atmospheric pressure and at 400-500 °C (673-773 K) in vacuo [2] are of great theoretical and practical interest. Possible decomposition of selenides, or lack thereof, and the sequence of such reactions can affect the stability of the construction material in respect to the selenium-containing melts.

Moreover, whereas the dissociation processes of ferrous, nickelous and cobaltous sulphides have been studied quite well [3 - 7], there are only few studies [8] devoted to decomposition of selenides of these metals. Besides, it should be noted that the thermodynamic research of the Co-Se \( \text{Ni-Se} \) systems have been reported only in few works [9-12], Fe-Se - in [8, 13, 14].

There are no direct methods of the selenides decomposition processes study in forevacuum developed to date. However, it is known that under nonequilibrium conditions the chemical processes take place in the same consequence as in achieving the equilibrium.

To evaluate the behavior of ferrous, nickelous and cobaltous selenides in the distillation process we used the partial pressure diagram method. We examined the thermodynamic equilibrium of ferrous triad selenides with different stoichiometric composition and vapor phase represented with selenium. Due to the fact that mass spectrometry analysis of vapor at atmospheric pressure of 672 °C (945 K) has been previously determined by us.

Experimental Part and Discussion of Results. Decomposition of Cobaltous Selenides. There are two molecular entities, i.e. \( \text{FeSe} \) selenite and ferrous diselenide in the Fe-Se phase diagram [18]. The partial pressure diagram (hereinafter) has been constructed in the coordinates \( \ln p_{\text{Se}_2} \), \( T \). We took the equilibrium between the crystalline \( \text{FeSe}_2 \), \( \text{FeSe}_2 \) (cryst), \( \text{FeSe}_{2(cr)} \) and gaseous \( \text{Se}_{2(g)} \) into account. The values of the thermodynamic functions of the condensed phases were taken from [19, 20], \( \text{Se}_{2(g)} \) - [21]. Possible reactions between constituents of the condensed and gas phases and the estimated values of the equilibrium
constants with the assumption that $\Delta H^\circ$ and $\Delta S^\circ$ are not dependent on the temperature, are given in Table 1.

Table 1 – Decomposition Reactions of Ferrous Selenides and Reaction Equilibrium Constants

<table>
<thead>
<tr>
<th>№</th>
<th>Reaction</th>
<th>$\ln K_p$ value at a temperature in K:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2 \text{FeSe}<em>{(cr)} = 2 \text{Fe}</em>{(cr)} + \text{Se}_2(g)$</td>
<td>$-32,119$ $-17,221$</td>
</tr>
<tr>
<td>2</td>
<td>$2 \text{FeSe}<em>{2(cr)} = 2 \text{FeSe}</em>{(cr)} + \text{Se}_2(g)$</td>
<td>$-14,796$ $-2,803$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{FeSe}<em>{2(cr)} = \text{Fe}</em>{(cr)} + \text{Se}_2(g)$</td>
<td>$-18,063$ $-4,618$</td>
</tr>
<tr>
<td>4</td>
<td>$3 \text{FeSe}<em>{2(cr)} = 2 \text{FeSe}</em>{(cr)} + \text{Fe}_{(cr)} + 2\text{Se}_2(g)$</td>
<td>$-61,236$ $-36,107$</td>
</tr>
</tbody>
</table>

The partial pressure diagram for ferrous selenide decomposition is shown in Figure 1. The numbers in the figure (hereinafter) correspond to the number of reactions in Table 1.

The diagram shows that in terms of selenium distillation from its melts in vacuum at ~673 - 803 K (400-530 °C) the thermodynamically stable phase of iron impurities is FeSe$_{2(cr)}$, diselenide, i.e. dissociation of the connection is not assumed. At ~803 K (determined graphically) to 945 K and 0.013-6.46 kPa (at corresponding temperatures) iron diselenide decomposition occurs under the reaction: $2 \text{FeSe}_{2(cr)} = 2 \text{FeSe}_{(cr)} + \text{Se}_2(g)$, with transfer of the selenium educed into the vapor phase. Decomposition of ferrous monoselenide in conditions of the selenium distillation from the melt both at atmospheric pressure and a vacuum is not possible.

Decomposition of Cobaltous Selenides. The Co - Se state diagram is made up to the concentration of 70 at. % of selenium. Three phases are formed in the system: Co$_9$Se$_8$, CoSe$_{(cr)}$, and CoSe$_{2(cr)}$ [18]. Co$_9$Se$_8$ Phase exists up to 500 °C and was not taken into account because of the lack of data on its thermodynamic properties.

We took the equilibrium between the crystalline Co$_{(cr)}$, CoSe$_{(cr)}$, CoSe$_{2(cr)}$, and gaseous Se$_2(g)$ into account. The values of the thermodynamic functions for the phases condensed were taken from [19, 20], Se$_2(g)$ - [21]. All possible reaction between the components of the condensed and gas phases and the calculated values of equilibrium constants are given in Table 2.

Table 2 – Decomposition Reactions of Cobaltous Selenides and Reaction Equilibrium Constants

<table>
<thead>
<tr>
<th>№</th>
<th>Reaction</th>
<th>$\ln K_p$ value at a temperature in K:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2 \text{CoSe}<em>{(cr)} = 2 \text{Co}</em>{(cr)} + \text{Se}_2(g)$</td>
<td>$-23,237$ $-10,491$</td>
</tr>
<tr>
<td>2</td>
<td>$2 \text{CoSe}<em>{2(cr)} = 2 \text{CoSe}</em>{(cr)} + \text{Se}_2(g)$</td>
<td>$-17,895$ $-6,828$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{CoSe}<em>{2(cr)} = \text{Co}</em>{(cr)} + \text{Se}_2(g)$</td>
<td>$-20,566$ $-8,659$</td>
</tr>
<tr>
<td>4</td>
<td>$3 \text{CoSe}<em>{2(cr)} = 2 \text{CoSe}</em>{(cr)} + \text{Co}_{(cr)} + 2\text{Se}_2(g)$</td>
<td>$-38,461$ $-15,488$</td>
</tr>
</tbody>
</table>

The partial pressure diagram for cobaltous selenide decomposition is shown in Figure 2.

The crystalline cobalt diselenide CoSe$_{2(cr)}$ is thermodynamically stable here, within the most part of the diagram field for technological conditions of the distillation process. The reaction (2, Table 2) of its dissociation with formation of CoSe$_{(cr)}$ monoselenide and vaporous selenium is possible only at temperatures ~ 880 K (607 °C) in the range of pressures 13-200 Pa. Cobaltous monoselenide decomposition in the conditions of distillation processes does not take place because the selenium vapor pressure at temperatures above 880 K (607 °C) greatly exceeds 200 Pa, and the temperature and the vapor pressure are interconnected, so to create a technological vacuum (200 Pa) at the indicated temperature (880 K) is not possible.

Decomposition of Nickelous Selenides. There are five compounds in the Ni - Se phase diagram [22]: Ni$_3$Se$_2$, Ni$_6$Se$_5$, Ni$_{21}$Se$_{20}$, NiSe and NiSe$_2$. Ni$_3$Se$_2$
The compound is formed by a peritectic reaction at 800 °C, Ni₅Se₁ and Ni₁₁Se₂₀ - by peritectoid reactions at 670 and 375 °C, Ni₅Se exists in the temperature range of 400-670 °C. The homogeneity field of the Ni₅Se compound melting congruently at 980 °C is about 50.5-56.5 at.% Se.

When we constructed the partial pressure diagram, we took the equilibrium between crystalline Ni₃Se₂(cr), Ni₅Se₂₀(cr), Ni₅Se₁₁(cr), and gaseous Se₂(g). The values of thermodynamic constants for condensed phases, except for Ni₅Se₂₀(cr), was taken from [19, 20], Se₂(g) from [21]. The change in enthalpy and entropy of Ni₃Se₂(cr) formation was defined approximately by the method of similar reactions due to the lack of data in the reference publications [23]. For the same reason, and because of the proximity of the stoichiometric composition of the compounds: Ni₅Se₁₁ - 45.5 at.% Se, Ni₁₁Se₂₀ - 48.8 at.% Se to nickelous monoselenide NiSe, the latter are not taken into account in the calculation of equilibrium reactions. The possible reaction with the assumptions made for constituents of condensed and gaseous phases and calculated values of the equilibrium constants are specified in Table 3.

Table 3 – Decomposition Reactions of Nickelous Selenides and Reaction Equilibrium Constants.

<table>
<thead>
<tr>
<th>№</th>
<th>Reaction</th>
<th>Ln Kp value at a temperature in K:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni₅Se → 3 Ni(cr) + Se₂(g)</td>
<td>673: -34,335, 945: -19,654</td>
</tr>
<tr>
<td>2</td>
<td>6 Ni₅Se → 2 Ni₃Se₂(cr) + Se₂(g)</td>
<td>673: -3,218, 945: 6,945</td>
</tr>
<tr>
<td>3</td>
<td>2 Ni₅Se → 2 NiSe(cr) + Se₂(g)</td>
<td>673: 6,849, 945: 14,602</td>
</tr>
<tr>
<td>4</td>
<td>2 Ni₅Se → 2 Ni(cr) + Se₂(g)</td>
<td>673: -24,033, 945: -10,836</td>
</tr>
<tr>
<td>5</td>
<td>Ni₅Se₂₀ → Ni₅Se + Se₂(g)</td>
<td>673: -14,816, 945: -4,341</td>
</tr>
<tr>
<td>6</td>
<td>4 Ni₅Se → Ni₅Se₂₀ + 3 Ni(cr) + Se₂(g)</td>
<td>673: -33,104, 945: -17,231</td>
</tr>
</tbody>
</table>

The partial pressure diagram for nickelous selenide decomposition is shown in Figure 3.

Based on the partial pressure diagram, the thermally stable nickel selenide under the conditions of the distillation process at atmospheric pressure (945 K, 101.3 kPa) and under vacuum (673-773 K, 13-1000 Pa) is Ni₅Se₁₁(cr). Nickelous monoselenide and diselenide are stable only at redundant pressures, i.e., more than 101.3 kPa (1 atm). Due to the similar behavior this is not consistent with the properties in the technological processes of nickelous sulfide and disulfide, where nickel monochal-cogenide is present in melts at the temperature above 1000 °C (1273 K) under atmospheric pressure.

In order to eliminate any possible errors in approximate determination of the thermodynamic properties the partial pressure diagram has been calculated without Ni₅Se₂₀(cr) compound (Figure 4).

The thermodynamically stable phase at atmospheric and low pressure in this case is a nickel monoselenide NiSe which corresponds to the usual behavior of nickel chalco-genides in technological processes. Decompensation of nickel diselenide Ni₅Se₂₁ to monoselenide is possible only at pressures much greater than atmospheric ones.

Such differences in the results of the dissociation analysis of selenides and the sequence of their occurrence demonstrate the need for studies to determine the thermodynamic constants of chalcogenides of different composition.

Conclusions. Thus, based on partial pressure diagram of iron, cobalt and nickel dissociation it was found out that in the conditions of vacuum and distillation selenium transfer to the vapor phase and at the presence of metal impurities in the melts, ferrous diselenide FeSe₂(cr), cobaltous monoselenide CoSe₂(cr), and nickelous monoselenide NiSe₂(cr) are thermodynamically stable. Increase of the process pressure to atmospheric pressure of 0.1 MPa does not change the composition and stability of the compounds.
In the process of distillation extraction of selenium from muddling products and element refinement, the iron, nickel and cobalt impurities will be concentrated in the bottoms as above mentioned selenides.

REFERENCES


