

S. A. TREBUKHOV*, V. N. VOLODIN, A. V. NITSENKO, N. M. BURABAEVA, A. A. TREBUKHOV

*Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan, * vohubert@mail.ru*

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 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 - CoSe_2 (crist.). At temperatures above 607 °C in the pressure range 13-200 Pa it is possible dissociation CoSe_2 (crist.) with formation of monoselenide CoSe (crist.) and selenium vapor. Nickel in the selenium melts at atmospheric and low pressures is presented in the form of a stable phase – nickel monoselenide 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 FeSe_2 (crist.), cobalt diselenide CoSe_2 (crist) and nickel monoselenide NiSe (crist.) 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 и 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 selenium sublimation and distillation [15, 16] has shown the predominant the presence of two molecules of Se_2 at the temperatures higher than 673 K, we considered that the vapor phase in the calculations consists of dimers, and the activity of the condensed phases is equal to one. The field of process parameters (highlighted in the figures) is limited with temperature range from 400 up to the selenium boiling point of 672 °C (673-945 K) and with pressures from $1,3 \cdot 10^{-4}$ up to 1 atm (13 – 101325 Pa) corresponding to the conditions of distillation processes under atmospheric and low pressures. The boiling point of selenium 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. FeSe selenite and ferrous diselenide in the Fe-Se phase diagram [18]. The partial pressure diagram (hereinafter) has been constructed in the coordinates $\ln p_{\text{Se}_2} - T^{-1}$. We took the equilibrium between the crystalline $\text{Fe}_{(\text{cr})}$, $\text{FeSe}_{(\text{cr})}$, $\text{FeSe}_{2(\text{cr})}$ and gaseous $\text{Se}_{2(\text{g})}$ into account. The values of the thermodynamic functions of the condensed phases were taken from [19, 20], $\text{Se}_{2(\text{g})}$ - [21]. Possible reactions between constituents of the condensed and gas phases and the estimated values of the equilibrium

constants with the assumption that ΔH° and ΔS° are not dependent on the temperature, are given in Table 1.

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

№	Reaction	Ln Kp value at a temperature in K:	
		673	945
1	$2 \text{FeSe}_{(cr)} = 2 \text{Fe}_{(cr)} + \text{Se}_{2(g)}$	-32,119	-17,221
2	$2 \text{FeSe}_{2(cr)} = 2 \text{FeSe}_{(cr)} + \text{Se}_{2(g)}$	-14,796	-2,803
3	$\text{FeSe}_{2(cr)} = \text{Fe}_{(cr)} + \text{Se}_{2(g)}$	-18,063	-4,618
4	$3 \text{FeSe}_{2(cr)} = 2 \text{FeSe}_{(cr)} + \text{Fe}_{(cr)} + 2\text{Se}_{2(g)}$	-61,236	-36,107

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.

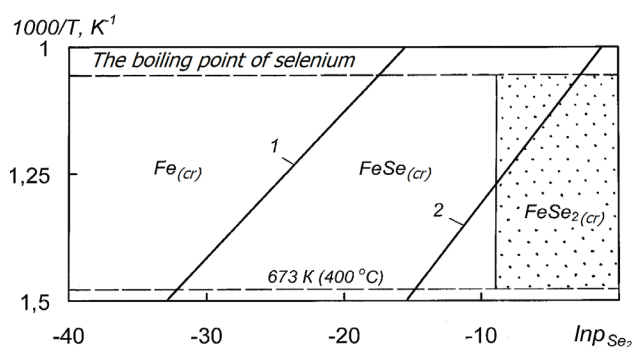


Figure 1 – Partial Pressure Diagram for Ferrous Selenide Decomposition.

The diagram shows that in terms of selenium distillation from its melts in vacuum at $\sim 673 - 803 \text{ K}$ ($400 - 530 \text{ }^\circ\text{C}$) the thermodynamically stable phase of iron impurities is $\text{FeSe}_{2(cr)}$ diselenide, i.e. dissociation of the connection is not assumed. At $\sim 803 \text{ K}$ (determined graphically) to 945 K and $0.013 - 6.46 \text{ kPa}$ (at corresponding temperatures) iron diselenide decomposition occurs under the reaction: $2 \text{FeSe}_{2(cr)} = 2 \text{FeSe}_{(cr)} + \text{Se}_{2(g)}$ to Fe monoselenide 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_9Se_8 , $\text{CoSe}(\gamma)$ and CoSe_2 [18]. Co_9Se_8 Phase exists up to $500 \text{ }^\circ\text{C}$ and was not taken into account because of the lack of data on its thermodynamic properties.

We took the equilibrium between the crystalline $\text{Co}_{(cr)}$, $\text{CoSe}_{(cr)}$, $\text{CoSe}_{2(cr)}$ and gaseous $\text{Se}_{2(g)}$ into account. The values of the thermodynamic functions for the phases condensed were taken from [19, 20], $\text{Se}_{2(g)}$ - [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

№	Reaction	Ln Kp value at a temperature in K:	
		673	945
1	$2 \text{CoSe}_{(cr)} = 2 \text{Co}_{(cr)} + \text{Se}_{2(g)}$	-23,237	-10,491
2	$2 \text{CoSe}_{2(cr)} = 2 \text{CoSe}_{(cr)} + \text{Se}_{2(g)}$	-17,895	-6,828
3	$\text{CoSe}_{2(cr)} = \text{Co}_{(cr)} + \text{Se}_{2(g)}$	-20,566	-8,659
4	$3 \text{CoSe}_{2(cr)} = 2 \text{CoSe}_{(cr)} + \text{Co}_{(cr)} + 2\text{Se}_{2(g)}$	-38,461	-15,488

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

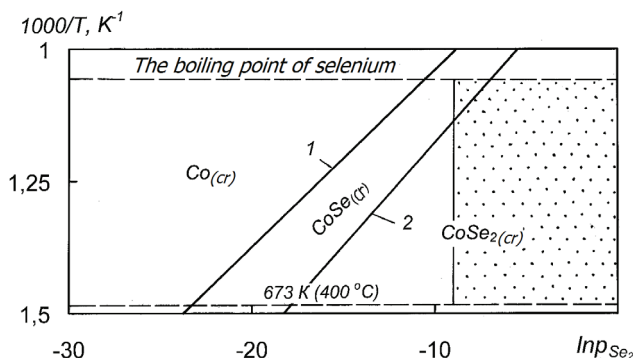


Figure 2 – Partial Pressure Diagram for Cobaltous Selenide Decomposition.

The crystalline cobalt diselenide $\text{CoSe}_{2(cr)}$ 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 $\text{CoSe}_{(cr)}$ monoselenide and vaporous selenium is possible only at temperatures $\sim 880 \text{ K}$ ($607 \text{ }^\circ\text{C}$) in the range of pressures $13 - 200 \text{ Pa}$. Cobaltous monoselenide decomposition in the conditions of distillation processes does not take place because the selenium vapor pressure at temperatures above 880 K ($607 \text{ }^\circ\text{C}$) 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_3Se_2 , Ni_6Se_3 , $\text{Ni}_{21}\text{Se}_{20}$, NiSe and NiSe_2 . Ni_3Se_2

compound is formed by a peritectic reaction at 800 °C, Ni₆Se₅ and Ni₂₁Se₂₀ - by peritectoid reactions at 670 and 375 °C, Ni₆Se₅ exists in the temperature range of 400-670 °C. The homogeneity field of the NiSe 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 Ni_(cr), Ni₃Se_{2(cr)}, NiSe_(cr), NiSe_{2(cr)} and gaseous Se_{2(g)}. The values of thermodynamic constants for condensed phases, except for Ni₃Se_{2(cr)}, was taken from [19, 20], Se_{2(g)} from [21]. The change in enthalpy and entropy of Ni₃Se_{2(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: Ni₆Se₅ – 45.5 at. % Se, Ni₂₁Se₂₀ – 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.

№	Reaction	Ln Kp value at a temperature in K:	
		673	945
1	Ni ₃ Se _{2(cr)} = 3 Ni _(cr) + Se _{2(g)}	-34,335	-19,654
2	6 NiSe _(cr) = 2 Ni ₃ Se _{2(cr)} + Se _{2(g)}	-3,218	6,945
3	2 NiSe _{2(cr)} = 2 NiSe _(cr) + Se _{2(g)}	6,849	14,602
4	2 NiSe _(cr) = 2 Ni _(cr) + Se _{2(g)}	-24,033	-10,836
5	NiSe _{2(cr)} = Ni _(cr) + Se _{2(g)}	-14,816	-4,341
6	4 NiSe _(cr) = NiSe _{2(cr)} + 3 Ni _(cr) + Se _{2(g)}	-33,104	-17,231

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

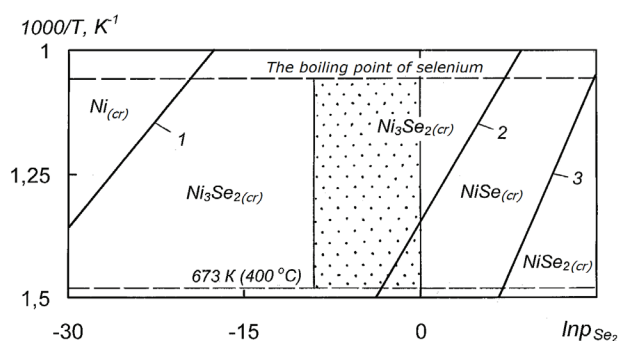


Figure 3 – Partial Pressure Diagram for Nickelous Selenide Decomposition

Based on the partial pressure diagram the thermally stable nickel selenide under the conditions of the distillation process at atmosphere pressure (945 K, 101.3 kPa) and under vacuum (673-773 K, 13-1000 Pa) is Ni₃Se_{2(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 monochalcogenide 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 Ni₃Se_{2(cr)} compound (Figure 4).

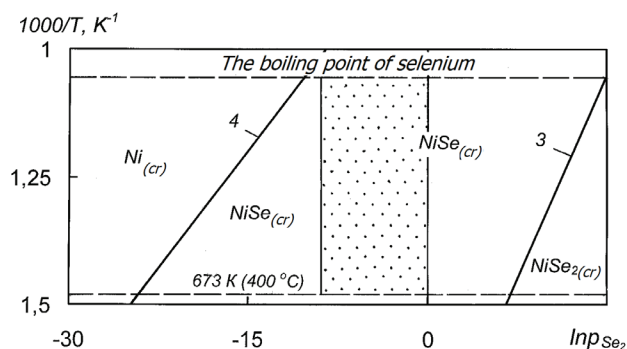


Figure 4 - Partial Pressure Diagram for Nickelous Selenide Decomposition without Ni₃Se_{2(cr)}

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 chalcogenides in technological processes. Decomposition of nickel diselenide NiSe₂ to monoselenide is possible only at pressures much greater than atmospheric ones.

Such difference in the results of the dissociation analysis of selenides and the sequence of their occurrence demonstrates 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 FeSe_{2(cr)}, cobaltous monoselenide CoSe_{2(cr)} and nickelous monoselenide NiSe_(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 middling products and element refinement, the iron, nickel and cobalt impurities will be concentrated in the bottoms as above mentioned selenides.

REFERENCES

- 1 V.N. Volodin, S.A. Trebukhov, N.M. Burabaeva, A.V. Nicenko, A. Kasymzhanova. *Fazovaya diagramma zhelezo – selen pri nizkom davlenii*. (Phase diagram of iron - selenium at low pressure). *Kompleksnoe ispol'zovanie mineral'nogo syr'ya = Complex Use of Mineral Resources*. **2016**. 3. 53 (in Russ.).
- 2 Isakova R.A., Reznikov A.A., Spivak M.M. *Rafinirovanie selen* (Selenium refining). Alma-Ata. Nauka. **1975**. 107 (in Russ.).
- 3 Isakova R.A., Nesterov V.N., Shendypin A.S. *Davlenie para i dissociaciya sul'fidov medi i nikelya* (The vapor pressure and the dissociation of metal sulphides). *Trudy instituta metallurgii i obogasheniya Akademii Nauk Kaz SSSR = Proceedings of the Institute of Metallurgy and Ore Benefication of the Academy of Science of Kazakh SSR*. **1963**. 6. 156-159 (in Russ.).
- 4 Isakova R.A. *Davlenie para i dissociaciya sul'fidov metallov* (The vapor pressure and the dissociation of metal sulphides). Alma-Ata. Nauka. **1968**. 230 (in Russ.).
- 5 Vanyukov A.V., Isakova R.A., Bystrov V.P. *Termicheskaya dissociaciya sul'fidov metallov* (Thermal dissociation of metal sulfides). Alma-Ata. Nauka. **1978**. 272 (in Russ.).
- 6 Lopatin S.I., Blatov I.A., Kharlanov A.S. *Issledovanie aktivnosti komponentov v sisteme Fe-S metodom vysokotemperaturnoj mass-spektrometrii* (Study of components activity in the Fe-S system by high-temperature mass spectrometry). *Metally = Metals*. **1999**. 5. 33-35 (in Russ.).
- 7 Morachevskij A.G., Ryabko A.G., Cemekhman L.Sh. *Termodinamika sistemy zhelezo-sera. Termodinamika sistem i processov v metallurgii nikelya i medi*. (Thermodynamics of the iron-sulfur system. Thermodynamics of systems and processes in metallurgy of nickel and copper). St. Petersburg: Politekhnic. universitet (Publisher Polytechnic University). **2005**. 155 (in Russ.).
- 8 Placente V., Scardala P., Fontana D. Decomposition pressure and standard enthalpies of sublimation and formation of iron monoselenide. *Journal Alloys and Compounds*. **1992**. 189. 2. 263-267 (in Eng.).
- 9 Feenberg I. Ya., Vajsburd S. E. *Termodinamicheskie svojstva rasplavov sistemy Co-Se* (Thermodynamic properties of Co-Se system melts). *Zhurnal fizicheskoi khimii = Journal of Physical Chemistry*. **1972**. 46. 6. 1575-1577 (in Russ.).
- 10 Feenberg I. Ya., Vajsburd S.E. *Termodinamicheskie svojstva rasplavov sistemy Ni-Se. Termodinamicheskie svojstva metallicheskih splavov* (Thermodynamic properties of Co-Se system melts. Thermodynamic properties of metal alloys). Baku: Ehlm. **1975**. 395-398 (in Russ.).
- 11 Morozova M.P., Vladimirova V.A., Grudekij A.V., Nikolaeva L. *Fiziko-khimicheskoe issledovanie sistemy Co-Se. Termodinamicheskie svojstva tverdykh metallicheskih splavov* (Physico-chemical study of the system Ce-Co is. Thermodynamic properties of solid metal alloys). Minsk: Belorusskij Gosudarstvennyj Universitet (Belarusian State University). **1976**. 140-142 (in Russ.).
- 12 Morozova M.P., Vladimirova V.A., Stolyarova T.A., Pavlinova L.A. *Fiziko-khimicheskoe issledovanie sul'fidov, telluridov i selenidov kobal'ta i nikelya v predelakh oblastej gomogenosti* (Physical and chemical research of sulphides, tellurides and selenides of cobalt and nickel in the range of homogeneity). *Khimiya i fizika hal'kogenidov* (Chemistry and physics chalcogenides). Kiev. Naukova dumka. **1977**. 52-54 (in Russ.).
- 13 Chizhikov D.M., Schastlivyj V.P. *Selen i selenidy* (Selenium and selenides) Moscow: Nauka. **1964**. 230 (in Russ.).
- 14 Sveshkov Yu.V., Alferov V.P., Kalmykov V.A., Vagin S.A. *Adsorbtsiya i poverkhnostnaya aktivnost' rastvora selen*

zhidkom zheleze (Adsorption and surface activity of the solution of selenium in the liquid iron) *Izvestiya Akademii nauk SSSR. Metally = Proceedings of the USSR Academy of Sciences. Metals*. **1973**. 6. 74-76 (in Russ.).

15 Goldfinger P., Jeunehomme M. Mass Spectrometric and Knudsen-Cell Vaporization Studies of group 2B-6B Compounds. *Transactions of the Faraday Society*. **1963**. 59, 12. 2851-2867 (in Eng.).

16 Gol'dfinger P., Dzhennom M. *Mass-spektrometricheskoe izuchenie termodinamicheskikh svojstv soedinenij jelementov III-V i II-VI grupp periodicheskoi sistemy* (Mass spectrometric study of the thermodynamic properties of compounds of elements of III-V and II-VI of the periodic system). *Uspekhi mass-spektrometrii* (Advances mass spectrometry) Moscow: Inostr. Literatura. **1963**. 521-530 (in Russ.).

17 Burabaeva N.M., Volodin V.N., Trebukhov S.A., Ersajnova A.A. *Termodinamika obrazovaniya i ispareniya splavov selen-sera* (Thermodynamics of formation and evaporation of sulfur-selenium alloys). *Kompleksnoe ispol'zovanie mineral'nogo syr'ya = Complex Use of Mineral Resources*. **2016**. 1. 48-53 (in Russ.).

18 Diagrammy sostoyaniya dvojnnykh metallicheskih sistem (The diagrams of binary metallic systems) *Spravochnik* (Directory). under the editorship of N.P. Lyakisheva Moscow. Mashinostroenie. **1997**. 2. 1024 (in Russ.)

19 Obolonchik V.A. *Selenidy* (Selenides). Moscow. Metallurgiya. **1972**. 296 (in Russ.)

20 *Termicheskie konstanty veshhestv* (Thermal constants of substances). *Spravochnik pod redakstej V.P. Glushko. Vserossijskij institut nauchnoj i tekhnicheskoi informacii* (Directory. Russian Institute for Scientific and Technical Information. under the editorship of V.P. Glushko). Moscow. **1972**. 6. 1. 369 (in Russ.)

21 Esirkegenov G.M., Valiev H.H., Spicyn V.A. *Issledovaniya razlozheniya selenidov medi i sostava parovoj fazy* (Research decomposition of copper sulphides and the composition of the vapor) *Metallurgiya i obogashchenie. Alma-Ata: Kazahskij Politehnicheskij Institut* (Metallurgy and enrichment. Alma-Ata: Kazakh Polytechnic Institute). **1975**. 10. 37-41 (in Russ.)

22 *Diagrammy sostoyaniya dvojnnykh metallicheskih sistem* (The diagrams of binary metallic systems) *Spravochnik pod redaktsiej N.P. Lyakisheva* (Directory under editorship of N.P. Lyakishev) Moscow: Mashinostroenie. **2000**. 3, 2. 448 (in Russ.).

23 Kireev V.A. *Metody prakticheskikh raschetov v termodinamike khimicheskikh reaktsij* (Methods of practical calculations in the thermodynamics of chemical reactions). Moscow: Khimiya (Chemistry) **1975**. 535 (in Russ.)

ЛИТЕРАТУРА

1 В.Н. Володин, С.А. Требухов, Н.М. Бурабаева, А.В. Ниценко, А. Касымжанова. Фазовая диаграмма железо – селен при низком давлении // КИМС. - 2016. - №3. - С.53-56.

2 Исакова Р.А., Резняков А.А., Спивак М.М. Рафинирование селена. – Алма-Ата, Наука. 1975. – 107 с.

3 Исакова Р.А., Нестеров В.Н., Шендяпин А.С. Давление пара и диссоциация сульфидов меди и никеля // Труды Института Metallurgii и Обогащения АН Каз ССР. -1963. - Т.6. - С.156-159.

4 Исакова Р.А. Давление пара и диссоциация сульфидов металлов. Алма-Ата: Наука. - 1968. - 230с.

5 Ванюков А.В., Исакова Р.А., Быстров В.П. Термическая диссоциация сульфидов металлов. – Алма-Ата: Наука. 1978. – 272 с.

6 Лопатин С.И., Блатов И.А., Харланов А.С. и др. Исследование активности компонентов в системе Fe-S методом высокотемпературной масс-спектрометрии // Металлы. - 1999. - №5. - С.33-35.

7 Морачевский А.Г., Рябко А.Г. Цемехман Л.Ш. Термодинамика системы железо-сера / Термодинамика

систем и процессов в металлургии никеля и меди. – С-Пб.: Политехнический университет. 2005. - 155с.

8 Placente V., Scardala P., Fontana D. Decomposition pressure and standard enthalpies of sublimation and formation of iron monoselenide // J. Alloys and Compounds. - 1992. - V.189. - №2. - P.263-267.

9 Феенберг И.Я., Вайсбурд С.Е. Термодинамические свойства расплавов системы Co-Se // Журнал физической химии. - 1972. - Т.46. - №6. - С.1575-1577.

10 Феенберг И.Я., Вайсбурд С.Е. Термодинамические свойства расплавов системы Ni-Se / Термодинамические свойства металлических сплавов. – Баку. Элм. 1975. - С.395-398.

11 Морозова М.П., Владимиров В.А., Грудецкий А.В., Николаева Л. Физико-химическое исследование системы Co-Se/ Термодинамические свойства твердых металлических сплавов. Минск. Белорусский Государственный Университет - 1976. - С.140-142.

12 Морозова М.П., Владимиров В.А., Столярова Т.А., Павлинова Л.А. Физико-химическое исследование сульфидов, теллуридов и селенидов кобальта и никеля в пределах областей гомогенности. Химия и физика халькогенидов. – Киев: Наукова думка. 1977. - С.52-54.

13 Чижигов Д.М., Счастливый В.П. Селен и селениды. – М.: Наука. 1964. - 230с.

14 Свешков Ю.В., Алферов В.П., Калмыков В.А., Вагин С.А. Адсорбция и поверхностная активность раствора селена в жидком железе// Известия Академии наук СССР. Металлы. - 1973. - №6. - С.74-76.

15 Goldfinger P., Jeunehomme M. Mass Spectrometric and Knudsen-Cell Vaporization Studies of group 2B-6B Compaunds // Trans. Farad. Soc. - 1963. - Vol.59. - №12. - P.2851-2867.

16 Гольдфингер П., Дженхом М. Масс-спектрометрическое изучение термодинамических свойств соединений элементов III-V и II-VI групп периодической системы. Успехи масс-спектрометрии. – М.: ИЛ. 1963. - С.521-530.

17 Бурабаева Н.М., Володин В.Н., Требухов С.А., Ерсайынова А.А. Термодинамика образования и испарения сплавов селен-сера // КИМС. - 2016. - №1. - С.48-53.

18 Диаграммы состояния двойных металлических систем: Справочник. Под ред. Лякишева Н.П. М.: Машиностроение. - 1997. - Т.2. - 1024с.

19 Оболончик В.А. Селениды. – М.: Металлургия. 1972. – 296 с.

20 Термические константы веществ. Справочник. Под ред. Глушко В.П. – М.: Всероссийский институт научной и технической информации ВИНТИ. 1972. - Вып.6. - Ч.1. - 369 с.

21 Есиркегенов Г.М., Валиев Х.Х., Спицын В.А. Исследования разложения селенидов меди и состава паровой фазы. Металлургия и обогащение. – Алма-Ата: Казахский Политехнический Институт. - 1975. - Вып.10. - С.37-41.

22 Диаграммы состояния двойных металлических систем: Справочник. Под ред. Лякишева Н.П. М.: Машиностроение. 2000. - Т.3. - Кн.2. – 448 с.

23 Киреев В.А. Методы практических расчетов в термодинамике химических реакций. – М.: Химия. 1975. - 535 с.

ТҮЙІНДЕМЕ

Парциалды қысымдардың диаграммаларын қолданып, селеннің қайнау температурасы 672 °С атмосфералық қысымда және 400-500 °С вакуумда жүргізілген дистилляциялы үрдістің жағдайында темір, никель және кобальт селенидтерінің тәртібі зерттелген. Вакуумда 400-530°С температурада селенді оның балқымаларынан дистилляциялау жағдайында, темір қоспасының термодинамикалық тұрақты фазасы диселенид $FeSe_{2(кр)}$ болып табылады, қосылыстың диссоциациясы қарастырылмаған. 530 °С-тан 672 °С дейін (біз анықтаған селеннің қайнау температурасы) және 0,013-6,46 кПа қысым жағдайында темірдің диселенид моноселенидке ыдырау жүреді, селен бу фазасына өтеді. Селенді балқымадан дистилляциялау жағдайында темірдің моноселенидің ыдырату мүмкін емес. Кобальттың қоспасы балқымада $CoSe_{2(кр)}$ кристаллды кобальт диселениді тұрақты фазасы түрінде көрсетілген. 607 °С жоғары температураларда 13-200 Па қысымда, диселенидтің диссоциациясы мүмкін, нәтижесінде монселенид түзіледі және селен бу фазасына өтеді. Никель селенді балқымаларда, атмосфералық және төмен қысымдарда тұрақты моноселенид $NiSe$ фазасымен көрсетілген, бұл технологиялық үрдістерде никель сульфидтеріне сәйкес келеді. Зерттеулердің нәтижесінде, балқымада темір, никель және кобальт қоспалары бар кезде селенді вакуумдистилляциялы бу фазасына өткізу жағдайында, темір диселениді $FeSe_{2(кр)}$, кобальт диселениді $CoSe_{2(кр)}$ және никель моноселениді $NiSe_{(кр)}$ тұрақты болып табылады. Технологиялық қысымды 0,1 МПа дейін жоғарылату қосылыстардың тұрақтылығы және құрамына әсер етпейді.

Түйінді сөздер: селен, темір, никель, кобальт, темір моноселениді, темір диселениді, кобальт моноселениді, кобальт диселениді, никель моноселениді, никель диселениді, парциалды қысымдар диаграммасы.

РЕЗЮМЕ

С использованием диаграмм парциальных давлений рассмотрено поведение селенидов железа, никеля и кобальта в условиях дистилляционного процесса, реализуемого при температурах кипения селена 672 °С при атмосферном давлении и 400-500 °С в вакууме. В условиях дистилляции селена из его расплавов в вакууме при 400-530 °С термодинамически устойчивой фазой существования примеси железа является диселенид $FeSe_{2(кр)}$, диссоциации соединения не предполагается. При температурах от 530 °С до 672 °С (температуры кипения селена, определенной нами) и давлениях 0,013-6,46 кПа протекает разложение диселенида железа до моноселенида Fe с переводом селена в паровую фазу. Разложение моноселенида железа в условиях дистилляции селена из расплава не вероятно. Примесь кобальта представлена в расплаве стабильной фазой кристаллического диселенида кобальта - $CoSe_{2(кр)}$. При температурах выше 607 °С в интервале давлений 13-200 Па возможна диссоциации $CoSe_{2(кр)}$ с образованием моноселенида $CoSe_{(кр)}$ и парообразного селена. Никель в селеновых расплавах при атмосферном и низких давлениях присутствует в виде стабильной фазы монселенид никеля $NiSe$, что аналогично поведению сульфидов никеля в технологических процессах. В результате установлено, что в условиях вакуумдистилляционного перевода селена в паровую фазу и присутствия примесей металлов триады железа в расплаве, термодинамически устойчивыми являются диселенид железа $FeSe_{2(кр)}$, диселенид кобальта $CoSe_{2(кр)}$ и моноселенид никеля $NiSe_{(кр)}$. Повышение технологического давления до атмосферного 0,1 МПа не изменяет состава и стабильности соединений.

Ключевые слова: селен, железо, никель, кобальт, моноселениды, диселениды, диаграмма парциальных давлений.

Received 03.10.2016.