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

*Institute of Metallurgy and Ore Benefication, Almaty, Kazakhstan, *e-mail: Nuri_eng@mail.ru*

INTERACTION OF ALLOYING METALS OF CONSTRUCTION STEELS WITH LIQUID AND VAPOROUS SELENIUM

Abstract: Based on the thermodynamic study of the interaction of selenium with alloying metals: nickel, titanium and chromium, it is established that these elements will form selenides of different composition in the liquid and vapor phases under the distillation process. The following order of dissolution in liquid selenium is suggested: chromium, nickel, iron, titanium. This will lead to a preferential transition of the elements standing in the row in front of the iron into liquid selenium and degradation of the structural material based on alloyed steel. On the basis of partial pressure diagrams of selenium in systems with iron and doping metals, it was established that titanium and chromium under conditions of distillation recovery and refining of selenium at low pressures will be represented by thermally stable higher selenides, nickel in liquid selenium by diselenide, in contact with the vapor phase, nickel monoselenide . Diagrams of the state of selenium systems with nickel and chromium are supplemented by phase transitions of liquid-vapor at a pressure of 100 Pa. The boundaries of the coexistence of liquid condensed and vapor phases are calculated assuming the existence of extremely dilute solutions of selenium in liquid nickel and crystalline chromium. The concentration of higher nickel and chromium selenides in the bottom residue during the distillation refining of selenium was confirmed. In the case of structural design, the use of a batch process is recommended due to the formation of a layer of selenides on the steel surface, which acts as a protective skull.

Key words: selenium, nickel, titanium, chromium, selenide, diselenide, melt, partial pressure diagram, state diagram

Introduction. Due to the high chemical activity of selenium with respect to alloyed steels, it seemed reasonable to trace the interaction of nickel, titanium and chromium (the main constituents in steel X18H10T) in liquid and vaporous selenium.

Due to the fact that the activities of these elements in solid iron solutions are not known, the interaction of selenium with each of the metals in the free state is considered. Because of the difficulties in the laboratory design of such studies, the method of thermodynamic calculations of the equilibrium constant of the selenide-selenium (liquid) system and the method of partial pressure diagrams, where selenium vapor is represented as the gas component, was used.

Distillation recovery of selenium from industrial products and its refining takes place at a temperature of 400-500 °C (673-773 K) in vacuum to 13 Pa and at a boiling point of 672 ° C (945 K), determined by us at atmospheric pressure [1, 2]. In this connection, the temperature range for the studies was chosen to be 673 - 945 K (400 - 672 °C), pressure $1.3 \cdot 10^{-5}$ - 0.1 MPa.

The thermodynamic constants for the calculations are borrowed from [3-5] and adopted independent on temperature. Missing values were found approximately, mainly by the method of the same type of compounds [6].

Calculation part and discussion of results. *Interaction of selenium with nickel.* Possible reversible reactions for the formation of nickel selenides in a liquid selenium bath and the equilibrium constant at the boundary temperatures of the interval are given in Table 1.

Table 1 - Equilibrium constants for the formation of nickel selenides in liquid selenium

System	Reactions of decomposition - formation of selenides	Values ln k_p at temperature, K	
		673	945
Ni - Se	$Se_{(liq)} + NiSe_{(crys)} = NiSe_{2(crys)}$	+0,090	**-0,566**
	$Se_{(liq)} + Ni_3Se_{2(crys)} = 3NiSe_{(crys)}$	**-1,125**	**-2,979**
	$2Se_{(liq)} + 3Ni_{(crys)} = Ni_3Se_{2(crys)}$	+28,833	+20,614
	$2Se_{(liq)} + Ni_{(crys)} = NiSe_{2(crys)}$	+9,326	+5,312
	$Se_{(liq)} + Ni_{(crys)} = NiSe_{(crys)}$	+9,236	+5,867

Analyzing the data in Table 1, it can be seen that under the distillation conditions, liquid selenium reacts with nickel to form stable selenides. The dissociation of nickel diselenide is possible at the boiling point of selenium at atmospheric pressure (945 K). The decomposition of nickel monoselenide on $Ni_3Se_{2(crys)}$ and $Se_{(liq)}$ is thermodynamically probable over the entire temperature range. That is, the formation of nickel monoselenide through the interaction of liquid selenium and $Ni_3Se_{2(crys)}$ under these conditions is not realized.

Thus, liquid selenium will interact with nickel, which is a doping element in iron, to form selenides of variable composition, which will be accompanied by degradation of the structural material.

The interaction of vaporous selenium with nickel was considered in detail in [7] and is not given here.

The most complete information on stable compounds in the metal-selenium system can be obtained on the basis of the equilibrium phase diagram, which includes the phase transition of the melt vapor and allows one to judge the interaction of nickel and selenium, as well as the composition of the phases formed.

When calculating the boundaries of the coexistence of melts and vapor, the boiling point was assumed to be equal to the temperature at which the sum of the partial pressures of the vapor components is 100 Pa, that is, the phase transition of the melt vapor, and the composition of the vapor phase was determined as the ratio of the partial pressure of the component to the total pressure.

Thermodynamic studies of the nickel-selenium system are few in number [8, 9]. The authors of [8] used the method of measuring the electromotive forces of concentration chains to determine the activity of nickel at a temperature of 1300 °C in the range 50-85 atom % Ni in the region of homogeneous melts. The data of this study were used by us in constructing a liquid-vapor phase transition. The activity of selenium in these solutions was calculated by integrating the Gibbs-Duhem equation.

In connection with low solubility, the liquid-vapor equilibrium is calculated assuming the existence of extremely dilute solutions of selenium in nickel. Due to the high boiling point of nickel, the calculation is performed for forquacuum conditions.

The vapor pressure of liquid nickel is borrowed from [10] and converted to the form: $\ln p_{Ni(liq)}[Pa] = 26{,}235 - 46572 \cdot T^{-1}$. The vapor pressure of selenium was determined by us earlier [1, 2] and in the calculations it is accepted the corresponding equation: $\ln p_{Se(liq)}[Pa] = 24{,}797 - 12540 \cdot T^{-1}$.

The boundaries of the field of coexistence of melts and paraffin selenium in the forequacuum of 100 Pa: the boiling point and the corresponding vapor composition in the Ni-Selenium state diagram [11] are shown in Figure 1.

Here, the areas of coexistence of melts and the vapor phase at atmospheric pressure and in a vacuum are partially superimposed on each other and on the area of existence of the condensed phases.

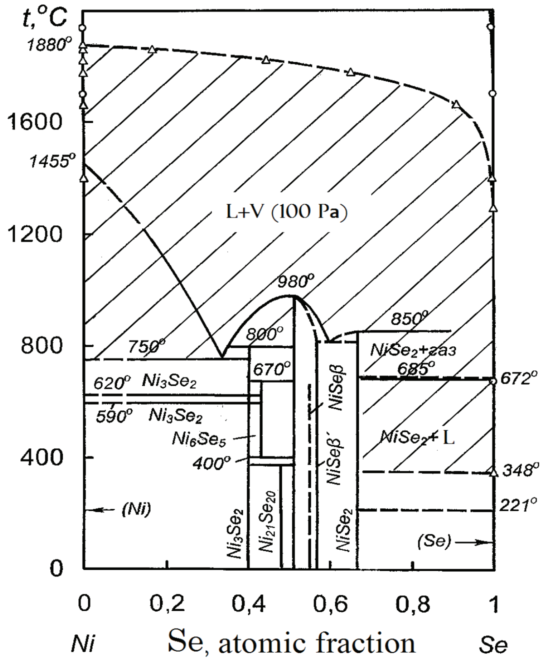

Figure 1 - Phase diagram of nickel-selenium at 100 Pa.

The vapor phase, almost completely, is represented by elemental selenium. Under the conditions of distillation separation of the system into components at low pressure, nickel will be concentrated in the bottom residue in the form of nickel diselenide. The durability of steels doped with nickel in the design of the technological process will be relatively low due to the formation of nickel diselenide in the interaction with liquid selenium and monoselenide with vapor Se [7].

Interactions of selenium with titanium and chromium. Possible reversible reactions for the formation of titanium and chromium selenides in a liquid selenium bath and the equilibrium constant at the boundary temperatures of the interval are given in Table 2.

Table 2 - Equilibrium constants of the reactions of formation of titanium and chromium selenides in liquid selenium

System	Reactions of decomposition-formation of selenides	Values of $\ln k_p$ at temperature, K	
		673	945
Ti – Se	$Ti_{(crys)} + Se_{(liq)} = TiSe_{(crys)}$	+40,261	+28,600
	$3TiSe_{(crys)} + Se_{(liq)} = Ti_3Se_{4(crys)}$	-67,323	-48,658
	$Ti_3Se_{4(crys)} + 2Se_{(liq)} = 3TiSe_{2(crys)}$	+155,55	+110,78
	$3Ti_{(crys)} + 4Se_{(liq)} = Ti_3Se_{4(crys)}$	+53,217	+37,889
	$Ti_{(crys)} + 2Se_{(liq)} = TiSe_{2(crys)}$	+69,589	+49,559
	$2TiSe_{(crys)} + Se_{(liq)} = 2TiSe_{2(crys)}$	+62,686	+39,692
Cr – Se	$2Cr_{(crys)} + 3Se_{(liq)} = Cr_2Se_{3(crys)}$	+25,514	+13,705

From the data in Table 2, it can be seen that, under distillation conditions, liquid selenium interacts with titanium and chromium to form stable selenides. Moreover, the formation of titanium diselenide from the elements, based on the value of the equilibrium constant, is more preferable. The formation of $Ti_3Se_{4(crys)}$ through the interaction of liquid selenium and titanium monoselenide under these conditions is not realized.

Thus, liquid selenium will interact with titanium and chromium, which are alloying elements in iron, to form selenides of variable composition, which will be accompanied by the destruction of the structural material.

Formation of selenides of titanium in a pair of selenium. The Ti-Se state diagram is not constructed [12]. Three compounds have been found in the system: TiSe, $TiSe_2$ and Ti_3Se_4.

Thermochemical studies are limited to work [4], in which, using the heat-conducting high-temperature calorimeter with an isothermal shell, the thermal effect of the direct synthesis reactions of the elements determines the standard enthalpies of formation of titanium selenides of variable composition $TiSe_x$, where x varies from 1.45 to 1.85. It is found that the dependence $\Delta H^o = f(x)$ corresponds to the equation of the line to find the enthalpy of formation of compounds due to the lack of data in the reference literature, we extended the concentration interval in this equation to $\Delta H^o = 156x + 64$. The values of entropy of formation are determined approximately by the additivity rule.

Possible reactions between the components of the condensed and gas phases and the calculated values of the logarithms of the equilibrium constants are given in Table 3.

Table 3 - Reactions and equilibrium constants of the reactions of formation of titanium selenides

№	Reactions	The values of ln k_p at temperature, K	
		673	945
1	$2\,Ti_{(crys)} + Se_{2(g)} = 2TiSe_{(crys)}$	+86,517	+56,733
2	$2TiSe_{(crys)} + Ti_{(crys)} + Se_{2(g)} = Ti_3Se_{4(crys)}$	-22,320	-20,777
3	$6TiSe_{(crys)} + Se_{2(g)} = 2Ti_3Se_{4(crys)}$	-131,157	-98,287
4	$Ti_3Se_{4(crys)} + Se_{2(g)} = 3TiSe_{2(crys)}$	+161,041	+109,807
5	$2TiSe_{(crys)} + Se_{2(g)} = 2TiSe_{2(crys)}$	+63,641	+40,442
6	$3Ti_{(crys)} + 2Se_{2(g)} = Ti_3Se_{4(crys)}$	+64,197	+35,956
7	$Ti_{(crys)} + Se_{2(g)} = TiSe_{2(crys)}$	+75,079	+48,588

In the partial pressure diagram (Figure 2), the only thermally stable phase at all temperatures within the range of 673 - 945 K (400 - 672 °C) and partial pressures of selenium from 13 Pa to atmospheric is crystalline titanium diselenide.

Here and below, the range of temperatures and pressures at which the distillation process is realized is isolated. The line numbers in the figure correspond to the number of the equilibrium reaction in Table 3.

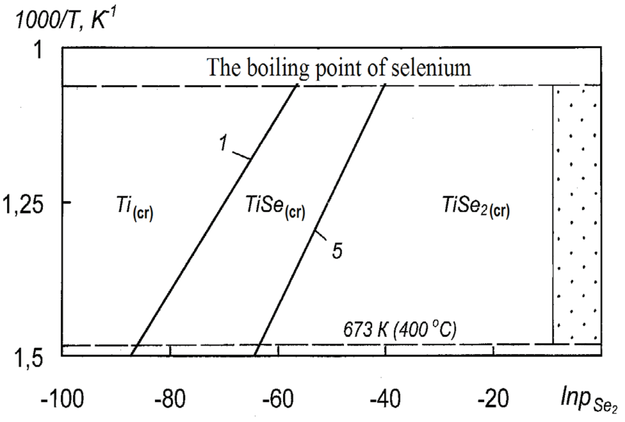

Figure 2 - The diagram of partial pressures $Ti_{(crys)} – Se_{2(g)}$

So, titanium, presented in steel as an alloying element, will interact with gaseous selenium to form titanium diselenide, which will promote chemical corrosion of the structural material. In the calculations of the equilibrium constant, if not available, the thermodynamic activity of titanium in the crystalline iron is not used, but this will not affect the formation of $TiSe_{2(crys)}$, since according to the scheme for the formation of selenides $Ti_{(crys)} \rightarrow TiSe_{(crys)} \rightarrow TiSe_{2(crys)}$ of the partial pressure of selenium, first of all, monoselenide of titanium is formed from the elements, the reaction of which must take into account the activity of the metal.

Formation - decomposition of chromium sesquieselenide in a selenium pair. In the system, in the concentration range ~ 50-60 at. % Selenium from the melt congruently formed compound, which is a disordered solid solution based on the compound $Cr_{1-x}Se$ [13]. Its melting point is between ~1550 and ~1500 °C, which corresponds to the boundary compositions of CrSe and Cr_2Se_3. With decreasing temperature, the disordered solid solution decays with the formation of ordered phases CrSe, Cr_3Se_4 and Cr_2Se_3 at 305, 911 and 811 °C. That is, under the conditions of the distillation process of extraction and refining of selenium, Cr_3Se_4 and Cr_2Se_3.

The thermodynamic functions of chromium selenides were determined only for sesquiselenide in the study [5], where the authors determined the enthalpy and entropy of the formation of γ-Cr_2Se_3. by the method of measuring electromotive forces of concentration galvanic cells at 140-220 °C. In this connection, in the construction of the partial pressure diagram, only the reaction of decomposition of chromium sesquieselenide into the initial elements is taken into account.

The thermally stable phase at temperatures and pressures typical for the processes of distillation of selenium will be $Cr_2Se_{3(crys)}$ (Figure 3).

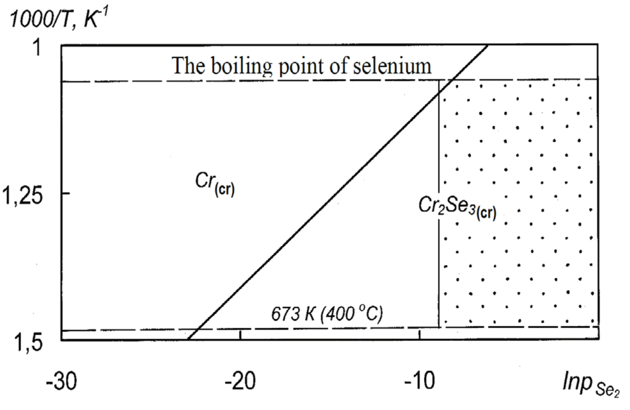

Figure 3. The diagram of the partial pressures of $Cr_{(crys)} – Se_{2(g)}$

Chromium presented in steel as an alloying element, interacts with gaseous selenium to form chromium sesquiselenide, which will promote chemical degradation of the structural material.

For more complete information on the formed and stable compounds in the chromium selenium system, an equilibrium state diagram including a phase transition of the melt-vapor.

In connection with the relatively high values of the vapor pressure of crystalline chromium and the small solubility of selenium in comparison with nickel and titanium, the calculation of the condensed phase-vapor equilibrium was carried out under the assumption of the existence of extremely dilute solutions of selenium in crystalline chromium. The vapor pressure of crystalline chromium is borrowed from [10] and converted to the form: $\ln p_{Cr\,(crys)}[Pa] = 29{,}173 - 41627 \cdot T^{-1}$.

The boundaries of the field of coexistence of the condensed phase (crystalline or liquid) and para selenium in the forequacuum of 100 Pa: the boiling point and its corresponding vapor composition are shown in Figure 4.

In the phase diagram, the region of existence of the vapor phase in vacuum is superimposed on the fields of existence of the condensed phases. The vapor phase, almost completely, is represented by elemental selenium. Under the conditions of distillation separation of the system into components at low pressure, chromium will interact with liquid selenium and concentrate in the bottom residue in the form of chromium sesquieselenide. The durability of chromium-doped steels will be relatively low due to the formation of this chromium selenide in the design of the process.

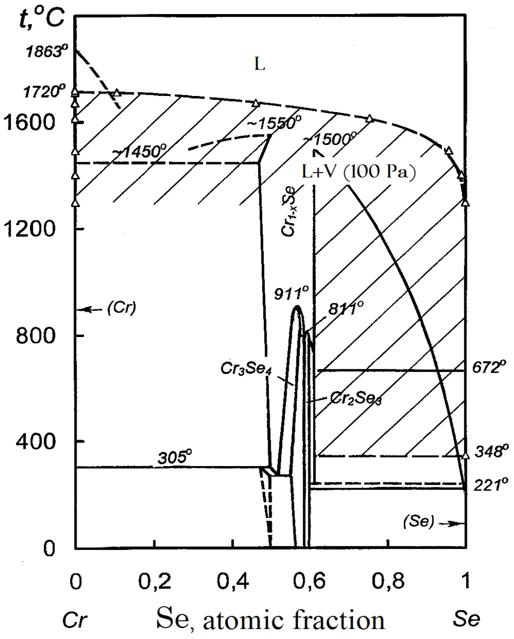

Figure 4 - Phase diagram of chromium – selenium at 100 Pa

Conclusions. Based on the thermodynamic study of the interaction of liquid and vaporous selenium with alloying metals: nickel, titanium and chromium, it is established that these elements in the melt will interact with selenium to form selenides.

On the basis of partial pressure diagrams of selenium in systems with alloying metals, it was established that titanium and chromium under the conditions of distillation recovery and refining of selenium at low pressures will be represented by thermally stable higher selenides, nickel in liquid selenium by diselenide, in contact with the vapor phase, nickel monoselenide.

Evaluating the organization of the technological distillation process in continuous and periodic modes in apparatuses made of alloy steel (X18N10T), preference should be given to periodic. This is due to the fact that in a continuous process, a continuous washout of the resulting selenides with a moving melt flow occurs and a shift in the equilibrium of the formation reactions toward the selenides. In the batch process the layer of selenides formed on the surface of the structural material plays the role of a protective skull.

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ТҮЙІНДЕМЕ

Легірлеуші никель, титан және хром сияқты металдармен селеннің өзара әрекеттесуінің термодинамикалық зерттеулерінің негізінде, аталған элементтер дистилляциялау үрдісі жағдайында сұйық және булы фазада әртүрлі құрамды селенидтер пайда болатындығы анықталды. Сұйық селенде ерудің болжамды кезектілігікелесідей: хром, никель, темір, титан. Бұл қатарда темірдің алдында тұрған элементтердің басымдықпен сұйық селенге өтуіне және негізі легірленген болат болатын конструкциялық материалдың құлдырауына әкеледі. Темір және легірлеуші металдар жүйелеріндегі селеннің парциалды қысым диаграммаларына негізделе төмен қысымда селенді дистилляциялық жағдайда шығарып алу мен тазалағанда титан мен хром термиялық тұрақты жоғары селенидтер түрінде, ал никель сұйық селенде диселенид түрінде және булы фазамен байланысқанда – никель моноселенид түрінде болатындығы анықталған. Селеннің никель мен хромды жүйесінің күй диаграммасы 100 Па қысымдағы сұйықтық-бу фазалық ауысуларымен толықтырылған. Сұйық конденсирленген және булы фазалардың қатар жүру шекаралары, кристалды хром мен сұйық никельді селен ерітінділерінің шегіне дейін араластырылғандағы тіршілік етуімен болжамдалып есептелген. Селенді дистилляциялық тазалаудағы кубтық қалдықта никель мен хромның жоғары селенидтер концентрациясы дәлелденген. Конструкторлық рәсімдеу кезінде қорғаушы гарниссаж рөлін орындайтын болат бетінде селенидтер қабатты пайда болатындықтан периодты үрдісті қолдану ұсынылған.

Түйінді сөздер: селен, никель, титан, хром, селенид, диселенид, балқыма, парциалды қысым дардиаграммасы, күй диаграммасы.

РЕЗЮМЕ

На основании термодинамического исследования взаимодействия селена с легирующими металлами: никелем, титаном и хромом установлено, что указанные элементы будут образовывать в условиях дистилляционного процесса селениды различного состава как в жидкой, так и паровой фазе. Предположена следующая очередность растворения в жидком селене: хром, никель, железо, титан. Это приведет к преимущественному переходу элементов, стоящих в ряду перед железом, в жидкий селен и деградации конструкционного материала на основе легированной стали. На основании диаграмм парциальных давлений селена в системах с железом и легирующими металлами установлено, что титан и хром в условиях дистилляционного извлечения и рафинирования селена при низких давлениях будут представлены термически устойчивыми высшими селенидами, никель в жидком селене диселенидом, при контакте с паровой фазой – моноселенидом никеля. Диаграммы состояния систем селена с никелем и хромом дополнены фазовыми переходами жидкость-пар при давлении 100 Па. Границы сосуществования жидкой конденсированной и паровой фаз рассчитаны в предположении существования предельно разбавленных растворов селена в жидком никеле и кристаллическом хроме. Подтверждена концентрация высших селенидов никеля и хрома в кубовом остатке при дистилляционном рафинировании селена. При конструктивном оформлении рекомендовано использование периодического процесса вследствие образования на поверхности стали слоя селенидов, выполняющего роль защитного гарниссажа.

Ключевые слова: селен, никель, титан, хром, селенид, диселенид, расплав, диаграмма парциальных давлений, диаграмма состояния

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