



Article Physicochemical Conditions of Boron–Siliconizing of Molybdenum-Based Alloys in Chlorine and Fluorine Medium

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Abstract: The physicochemical conditions of the siliconizing and boron–siliconizing processes of molybdenum-based alloys in a closed reaction space in an environment of chlorine and fluorine at reduced pressure were studied. Theoretical calculations of the equilibrium composition of systems with the participation of silicon, boron, molybdenum, nitrogen, oxygen, chlorine, and fluorine were carried out, which made it possible to determine the influence of process parameters (temperature, composition of the reaction medium) on the probable phase composition of the obtained coatings. Based on thermodynamic calculations, the composition and rational consumption of the initial powders and the temperature intervals of the chemical heat treatment (CHT) during the complex saturation of molybdenum-based alloys with silicon and boron were modeled. It was established that it is advisable to use chlorine as an activator, which leads to the formation of molybdenum chlorides MoCl₄ and MoCl₃ in the composition of the gas phase and can indicate the flow of exchange reactions between chlorides and the matrix of the processed material in the reaction space. The rational saturation temperature of alloys based on molybdenum with silicon and boron is determined—1100–1250 °C. The possibility of the existence of condensed phases MoSi₂, MoB_{2.15}, B₆Si, MoB_{1.65}, and MoB is shown.

Keywords: thermodynamics; gas phase; condensed phase; partial pressure; process innovation; industrial growth

1. Introduction

Research on alloys based on refractory metals, such as molybdenum, is of active interest due to the possibility of manufacturing parts from them that operate at temperatures above 1300 °C. However, molybdenum undergoes severe destruction at temperatures above 730 °C [1]. The problem of increasing heat resistance is solved in several ways: by alloying



Citation: Loskutova, T.; Scheffler, M.; Ivanov, V.; Pohrebova, I.; Kononenko, Y.; Bobina, M.; Kharchenko, N.; Bartoszuk, M.; Pavlenko, I. Physicochemical Conditions of Boron–Siliconizing of Molybdenum-Based Alloys in Chlorine and Fluorine Medium. *Metals* **2024**, *14*, 302. https://doi.org/ 10.3390/met14030302

Academic Editor: Changming Fang

Received: 18 January 2024 Revised: 27 February 2024 Accepted: 28 February 2024 Published: 3 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). alloys with elements that can form stable, protective films during oxidation [1-4], by applying protective coatings [5-7], or by a combined method. The most promising and realistic way to solve the heat resistance problem is using coatings. The most common type of high-temperature protective coatings are coatings with the participation of silicon, the high heat resistance of which is explained by the ability to form a surface oxide film based on SiO₂ [1,5-7].

A promising method for obtaining coatings from the gas phase is based on the production of diffusible elements in the atomic state from a chemical compound that exists in a gaseous state when it interacts with the heated surface of the workpiece. The diffusing element is transported to the surface to be treated as a chemical compound. The adsorption of this element is carried out after chemical reactions, either at the interface "gas phase–saturating surface" or in the volume of the gas phase. The chemical compounds used as transporters and suppliers of diffusing elements are halides, carbonyls, and organic compounds. The process is carried out at temperatures of 900–1500 °C for 2–50 h [8,9].

Paper [10] reports the results of studies of the process of complex boron–siliconizing of molybdenum-based alloys of the Mo-Si-B system. The process was carried out in a saturating mixture (70% wt. Al_2O_3 , 5% wt. NaF, and 25% wt. mixture of Si and B powders) at a temperature of 900 °C for 48 h in an argon environment. The obtained coatings were determined to consist of phases based on MoSi₂ and MoB [10].

In [11], the Mo-Si-B coating was applied to the Mo-6Si-12B-4Al-20Ti alloy in two successive stages. The pre-coating was applied to the molybdenum by spraying a suspension using a laboratory airbrush in the first stage. The suspension was prepared by mixing Mo powder in ethanol with 2.0% wt. hydroxypropyl cellulose as a binder. The Mo pre-coated sample was air-dried and then sintered at 1750 °C (with a heating/cooling rate of 15 °C/min) for 2 h in a high vacuum (< 1×10^{-5} bar). The second stage of the complex borosiliconization process was carried out in a saturating mixture of 62.5% wt., 34.03% wt. Si, 0.97% wt. B, 2.5% wt. NaF. The process was carried out at 1000 °C for 50 h in an argon environment. The obtained coatings were determined to consist of phases based on MoSi₂ and MoB [11].

Some research groups focus on the deposition of Si on Mo or Mo-based alloys by halide activated pack cementation (HAPC) [12]. The silicide coatings were applied to the surface of Mo-Si-B alloys at 1100 °C for 48 h. It was found that a 58 μ m thick MoSi₂-based layer was formed on the surface of the samples. A layer based on MoB₂ with a thickness of 6 μ m is directly adjacent to the base. This layer performs barrier functions and prevents silicon diffusion into the substrate matrix. It should be noted that this layer is not found in alloys with a low boron content [13].

Mathematical modeling is a powerful tool in modern materials science. Most often, models that are based on the methods of mathematical analysis of the equations of the classical theory of diffusion and quasi-equilibrium diffusion kinetics, mathematical statistics, and thermodynamic analysis are used [8]. Modeling the equilibrium state of the system using methods of thermodynamic analysis allows [8] the calculation of phase diagrams of equilibrium systems, which enables choosing the composition of the saturated alloy, shows the phase transformations that occur during heating and cooling; calculates the Gibbs energy and equilibrium constants of each chemical reaction and equilibrium concentrations (activity, partial pressure) of reactants and products in a saturated medium; determines the equilibrium composition of the gas phase in the reaction medium; and predicts the probability of formation of certain phases in the diffusion layer. The task of predicting the structure and properties of surface layers on metals after diffusion saturation with two or more elements currently needs to be solved. There is a process of accumulating and generalizing experimental material to establish general patterns. The task is complicated by the fact that empirical studies are conducted mainly with the use of powder mixtures, in which, during simultaneous saturation with several chemical elements, both the interaction of each element with the saturated metal and the interaction of the saturating elements with each other and with the activator are observed.

Mathematical modeling makes it possible to reduce the number of experiments and obtain the necessary experimental data in a shorter time and with lower costs. In addition, these theoretical calculations allow for optimizing the composition of saturating media and the molybdenum chemical heat treatment (CHT) technology parameters to obtain the best result (given the phase composition of the diffusion layer's optimal set of operational properties).

Computational thermodynamic approaches using the CALPHAD approach (calculation of phase diagrams) are widely used, and allow you to calculate equilibrium and metastable phase transformations based on a set of mutually agreed thermodynamic parameters of system phases [14]. The thermodynamic properties of each phase that takes part in the transformations are described by appropriate models, which for phases of constant composition should take into account the temperature dependence, and, in addition, for phases that have a region of homogeneity, the temperature-concentration dependence of the Gibbs energy [15]. This approach was used to model the behavior of the multicomponent reacting systems Nb-Ni-Si [16], Cr-Mn-Si [17], C-Nb-Mo [18], B-Fe-Ti [19], B-Mo-Ti [20], B-Mo-Nb [21], V-Ti-B [22], and many others, and allowed modeling of the corresponding state diagrams. The CALPHAD method is the mathematical basis of software products such as "Thermo-Calc", "JMathPro", "Pandat", "Pycalphad", etc. These software products have been widely used for computer modeling of structure formation in multicomponent systems, for example, for building state phase diagrams based on Scheil-Gulliver simulation. Thus, with the help of the program "Thermo-Calc" in work [23], state diagrams of multicomponent "hybrid" alloys of the Fe-C-B-W-Mo-V-Cr-Ti system were obtained and described, when the carbon and boron content varied within 0.3–1.1% and 1.5–3.5%, respectively. Halfa et al. [24] used this approach to predict the effect of vanadium on phase-structural transformations during the equilibrium crystallization of high-speed tool steel (Fe-C-W-Mo-V-Cr-Si system). The combination of the CALPHAD approach and the Johnson–Mehl–Avrami–Kolmogorov model allows for the simulation of solid-phase transformations. This simulation provides an opportunity to develop heat treatment modes of steels and cast irons [25].

The issue of using thermodynamic analysis to predict the structure and properties of surface layers on metals after diffusion saturation with two or more elements is currently unresolved. There is a process of accumulating and generalizing experimental material to establish general patterns. The task is complicated because experimental studies are mainly conducted using powder mixtures, in which, during simultaneous saturation with several elements, the interaction of each element with the saturated metal and the interaction of the saturating elements with each other and with the activator are observed.

It is known that, during the application of diffusion coatings, mass exchange occurs between the material being processed and the active medium formed in the reaction space during chemical heat treatment. At the same time, chemical reactions associated with mass exchange occur [9,26,27]. The flow of chemical reactions is possible simultaneously and sequentially, in the volume of the gas phase, at the interface with the material being processed, and even in the volume of the material itself. Data on mass transfer are obtained by studying chemical reactions in the reaction space and determining the drivers among them. This allows for influencing individual stages of the saturation process, determining optimal compositions of reaction media, and, finally, creating a justified technological process for obtaining protective coatings with predetermined properties.

Thus, the rational compositions of the original saturating medium can be determined based on analyzing chemical reactions that occur during chemical heat treatment and identifying leading reactions.

Works [8,9,26] show that, for a complete analysis of saturation processes, it is advisable to determine the equilibrium composition of the gas phase in a wide temperature range, including saturation temperatures. The obtained thermodynamic calculations make it possible to determine the process's principle possibility and select some technological parameters (temperature, pressure, concentration of components in the initial mixture). It

In many works, the software is used to determine the probable phase composition of coatings and saturating medium, the calculations of which are based on the entropy estimation of the closed system in works [9,26–28]. According to the second law of thermodynamics, the system with the minimum Gibbs energy or the maximum entropy will be thermodynamically advantageous among all possible systems. The program's data bank contains information on the thermodynamic characteristics of many substances. Calculations are carried out over a wide range of temperatures and pressures to determine the thermodynamic properties of the working body: total enthalpy, entropy, equilibrium heat capacity, etc.

In works [8,9,26], the physicochemical basis of applying one-component and twocomponent coatings based on carbides of transition metals on the surface of steels and hard alloys was investigated. Based on the data of thermodynamic analysis of chemical reactions occurring in the reaction space, methods and compositions of starting reagents for applying carbide coatings to the surface of steels and alloys in a closed reaction space at a reduced pressure of the active gas phase have been developed. A research study [29] considered the physical and chemical conditions of complex titanochromization of technical iron. The main chemical reactions taking place in the reaction space, the recommended compositions, and saturation temperature intervals were determined based on thermodynamic calculations.

In [30], a thermodynamic analysis was performed to determine the most likely phase composition of the polysilazane-type coating system on the Mo-Mo₃Si(A15)-Mo₅SiB₂(T2) alloy. The free Gibbs energy of chemical reactions between these constituents and resulting phases was calculated. In the phase equilibrium between the gas phase and condensed particles of the proposed coating system, nitrides, silicon oxynitrides, and molybdenum silicides were found. These compounds provide an increase in the heat resistance of Mo-Si-B-based alloys.

When analyzing diffusion saturation processes, the authors [31] considered the gas phase's interaction with the phases in the condensed state. The temperature and concentration regions of the stable existence of solid solutions of saturating metals in Fe-Me-O, Fe-Me-Cl, Fe-Me-Cl, Fe-Me-Cl-H-O-C, etc. systems were determined. The analysis of thermodynamic calculations in these works allowed the authors to approach the development of coating methods correctly, with predicted phase composition and properties.

Despite significant work in this area, clearly defined recommendations on the technological parameters of complex boron–siliconizing alloys must be made.

The analysis of the results of the study of physical and chemical conditions of siliconizing and boron–siliconizing in a chlorine/fluorine environment will allow a correct approach to the development of new methods for obtaining coatings of molybdenum with the required phase composition and properties. The knowledge of the rational ratio of silicon and boron powders and activator, as well as the heating temperature of the mixture and the material to be processed, allows us to justify the choice of technological parameters for the process of complex saturation of molybdenum-based alloys with silicon and boron. Therefore, for a justified choice of technological parameters of complex saturation of alloys based on molybdenum with silicon and boron, based on thermodynamic calculations, the equilibrium composition of the reaction medium under the accepted conditions of the process was studied, and the leading chemical reactions occurring in the chlorine environment were determined.

The paper aims to study the physical and chemical conditions of siliconizing and boronsiliconizing of alloys based on molybdenum in an environment with the participation of chlorine and fluorine in a closed reaction space under reduced pressure conditions, and the effect on phase composition of multicomponent coatings. Therefore, the paper is organized in the following structure. Section 1 provides the background and research topicality. The research methodology for the proposed research is described in detail in Section 2. The obtained results are presented and explained in Section 3. Results. The comparative study of the results is analyzed in Section 4. Discussion, where the achieved scientific results are compared with similar studies by other scientists. The scientific novelty and practical relevance of the research, significant results, and future plans are outlined in Section 5. Conclusions.

2. Materials and Methods

It is known [19] that the application of diffusion coatings is accompanied by mass transfer between the processed material and the active gas medium formed in the reaction space. This is because specific chemical reactions occur in a single system (active gas medium and processed material). These reactions take place simultaneously or sequentially. They are implemented in the volume of the gas phase, at the interface between the gas phase and the processed material, as well as inside the processed material. These reactions affect the coating formation process. The transition of the diffusing element from the active gas phase to the processed material, i.e., the process at the phase interface, is important for mass transfer.

When applying coatings in a closed reaction space using powders of saturating components (Si, B) and an activator (NH₄Cl, CCl₄, NiCl₂) as starting reagents, the main stages of mass transfer can be distinguished [9]:

- 1. As a result of the activator dissociation reactions, chlorine is released in free form;
- 2. Chlorine interacts with the saturating components, and chlorides of different stoichiometry (SiCl, SiCl₂, SiCl₃, SiCl₄, BCl, BCl₂, BCl₃, B₂Cl₄) are formed, due to which the saturating component is transferred to the surface of the samples. Mass transfer of saturating components from the reaction medium to the saturating surface is impossible without the formation of silicon and boron subchlorides [8];
- 3. Chemical reactions on the heated surface of the material to be treated, which are accompanied by the release of the saturating element in the atomic state and the removal of other reaction products into the gas phase;
- 4. Adsorption of the saturating element by the surface of the material to be treated;
- 5. Interaction of the diffusing element with the components of the material to be treated, accompanied by the formation of solid solutions or chemical compounds.

Intermediate reactions have not been presented in this paper. Only the final most thermodynamically probable chemical reactions are presented in this work.

To predict the course of the mass transfer process, its total dependence can be imagined in the following form (Equtation (1)) [8,9]:

$$m_i = \beta(\mu_i^R - \mu_i^M),\tag{1}$$

where m_i —the amount of matter transferred in the system per unit of surface per unit of time; β —total mass transfer coefficient; μ_i^R —chemical potential of a substance in the gas phase; and μ_i^M —chemical potential of the substance in the base material.

Chemical and physical factors affect the rate of mass exchange [9]. Therefore, data on mass transfer are obtained through a detailed study of the chemical reactions occurring in the reaction space and determination of the leading ones from among them. This makes it possible to find ways of influencing individual stages of the chemical–thermal treatment process to improve it, develop rational compositions of reaction media, and create a scientifically based technology for obtaining protective coatings with specified properties [9].

The main parameter that determines the ability of a chemical reaction to proceed under certain conditions of the process is the change in the thermodynamic potential. The most probable is the course of reactions with a more negative thermodynamic potential [8,9].

The change in the thermodynamic potential, ΔG_0 , of chemical reactions was calculated using the method [9]. These calculations make it possible to determine the most likely reactions of silicide formation. The main parameter that determines the equilibrium of the system, as well as its thermodynamic probability, is the value of the Gibbs energy, or the isothermal–isobaric potential, ΔG_T^0 , which was calculated according to the Equation (2):

$$\Delta G_T^0 = \Delta H_T^0 - T \Delta S_T^0, \tag{2}$$

where ΔH_T^0 —enthalpy change of initial and final reaction products in the standard state; *T*—temperature, K; and ΔS_T^0 —entropy change of initial and final reaction products in the standard state.

The probability of more than 100 exchange-type reactions was established during the interaction of chlorides of saturating elements (Si, B) with the base element (Mo) in the gas phase. When calculating thermodynamic reactions, we used the values of thermodynamic characteristics available in the HSC Chemistry 7.16 (Outotec Oy, Pori, Finland) program.

This paper analyzes the physicochemical conditions of saturation for a reasoned choice of technological parameters for applying diffusion coatings (ratio of starting metal powders, amount of halide, process temperature). This analysis is based on a thermodynamic approach aimed at the theoretical determination of the equilibrium state of the reaction medium. In this case, the quasi-equilibrium approximation was used to determine the limiting partial pressures. It is based on the assumption that, in the formation zones of the active gas phase and in the saturation zones, the pressure of gas components and the number of condensed phases are close to the values corresponding to equilibrium conditions. Theoretical studies of the physical and chemical conditions of coating application allow the solving of the following tasks: to determine the equilibrium composition of the reaction medium in the gas phase and condensed states; and to evaluate the influence of base components, air oxygen, and air nitrogen on the composition of the reaction medium [9].

The method of analyzing the thermodynamic equilibrium between different components of a heterophase multicomponent system was used to determine the composition of the reaction medium. The method is based on the derivative of the second law of thermodynamics [9]. Programs "Astra. 4" and "HSC Chemistry 7.16" (Outotec Oy, Pori, Finland), with a database of thermodynamic data, were used for calculations of the package of the application. As a result, the search for the equilibrium composition of the closed system with maximum entropy was carried out (Equation (3)):

$$S = \sum_{i} S_{i}^{0} n_{i} + \sum_{k} (S_{k}^{0} - R \ln p_{k}) n_{k} + \sum_{j} (S_{j}^{0} - R \ln x_{j}) n_{j} \to S_{\max}$$
(3)

where *i*, *k*, *j* are indices that belong to condensed phases, gases, and solution components; *n*—number of moles; *x*—concentration of substances; and *p*—partial pressure.

Equilibrium was evaluated in the temperature range typical for chemical and thermal treatment—200...1400 °C [8] for systems containing saturating elements—silicon and boron in different proportions, the basic element—molybdenum, components included in the composition of air—oxygen and nitrogen, as well as activator components—chlorine or fluorine. More than 150 variants of the Cl-Si-B-Mo and F-Si-B-Mo systems in the temperature range of 200–1400 °C were calculated in this work. The amount of chlorine (fluorine), silicon, boron, and molybdenum in the systems varied from 0.1 to 1.0 mol. During the calculations, the pressure in the reaction chamber was constant and equal to 10^2 Pa.

The performed calculations allow us to determine the quenching reactions occurring during the simultaneous saturation of molybdenum-based alloys with silicon and boron. The analysis of the equilibrium composition of the systems allows us to determine the influence of the temperature and the design of the initial components on the partial pressures of chlorides and fluorides of saturating metals. The composition of condensed substances corresponds to the probable composition of the surface area of the coating.

The work analyzed the most likely reactions during complex boron–siliconizing of molybdenum-based alloys in a chlorine environment. The equilibrium compositions of

the gaseous and condensed phases of the Cl-Si-B-Mo, F-Si-B-Mo systems of different compositions at 200–1400 $^\circ C$ temperatures were studied.

The possibility of complex saturation of alloys based on molybdenum with silicon and boron is estimated by the partial pressure of silicon and boron chlorides, and the phase composition of condensed substances at saturation temperatures. The composition of the coating, which is formed as a result of saturation, is determined by the phase composition of the condensed phases.

3. Results

It was established that the following reactions are the most thermodynamically probable under the assumed conditions of saturation and the presence of chlorine in the reaction space:

- 1. $2SiCl(g) + SiCl_2(g) + 3BCl_2(g) + 5Mo = MoSi_2 + SiCl_4(g) + MoB + MoB_2 + 2MoCl_3(g);$
- 2. $\operatorname{SiCl}_3(g) + 2\operatorname{SiCl}_2(g) + 3\operatorname{BCl}_2(g) + 6\operatorname{Mo} = \operatorname{MoSi}_2 + \operatorname{SiCl}_4(g) + \operatorname{MoB} + \operatorname{MoB}_2 + 3\operatorname{MoCl}_3(g);$
- 3. $2\operatorname{SiCl}(g) + \operatorname{SiCl}_2(g) + 2\operatorname{BCl}_2(g) + 4\operatorname{Mo} = \operatorname{MoSi}_2 + \operatorname{SiCl}_4(g) + 2\operatorname{MoB} + \operatorname{MoCl}_4(g);$
- 4. $2\operatorname{SiCl}_3(g) + \operatorname{SiCl}_2(g) + 2\operatorname{BCl}_2(g) + 5\operatorname{Mo} = \operatorname{MoSi}_2 + \operatorname{SiCl}_4(g) + 2\operatorname{MoB} + 2\operatorname{MoCl}_4(g);$
- 5. $2SiCl_3(g) + SiCl_2(g) + 3BCl_2(g) + 5.5Mo = MoSi_2 + SiCl_4(g) + MoB + MoB_2 + 2.5MoCl_4(g);$
- 6. $2\text{SiCl}_2(g) + 3\text{SiCl}_3(g) + BOCl(g) + N_2(g) + 4.5\text{Mo} = \text{MoSi}_2 + \text{SiCl}_4(g) + \text{MoB} + \text{Si}_2\text{N}_2\text{O} + 2.5\text{MoCl}_4(g)$

The possibility of the exchange-type reactions mentioned above is confirmed by the data of calculations of changes in the thermodynamic potential of these reactions (Figure 1). It was determined that the most likely chemical reactions are reactions (1) and (3), involving silicon monochloride, SiCl, silicon dichloride, SiCl₂, and boron dichloride, BCl₂.



Figure 1. Change in the free energy of the most probable reactions occurring during molybdenum boron–siliconizing depending on temperature.

These reactions can be considered the main ones during the boron–siliconizing of molybdenum. Reactions 2, 4, and 5 are also possible, in which silicon trichloride, SiCl₃, takes part instead of silicon monochloride, SiCl. All calculations are carried out assuming thermodynamic equilibrium for a chemically reacting system. Still, the system is in "mov-ing" thermodynamic equilibrium, and other chemical interactions do not stop in it, so these reactions are also possible when the conditions change.

As a result of reactions (1–5), molybdenum disilicide, MoSi₂, and molybdenum boron, MoB, MoB₂, should be formed in the products.

The participation of BOCl oxychloride in the gaseous environment (Reaction 6) shifts the temperature interval to lower values (Figure 1). The determined effect will allow the

adjustment of the temperature–time mode of saturation of molybdenum with silicon and boron during the experiment. Also, the compound Si_2N_2O appears in the reaction products.

The transfer of chlorides (fluorides) of silicon and boron to the surface of molybdenum alloys is possible due to the difference in their specific masses and vapor elasticity. The equilibrium composition of the reaction medium was calculated based on the following requirements [9]:

- The partial pressure of chlorides of saturating elements (silicon, boron, etc.) must be sufficiently high; the difference in the partial pressures of the halides (chlorides, fluorides) of the saturating elements should not be significant;
- Substances that correspond to the type of coating being applied are present among the condensed phases;
- Silicon and boron halides (chlorides, fluorides) of different valence must be present in the gas phase, which makes it likely that reverse disproportionation transport reactions will occur in the reaction space;
- The content of ballast and harmful substances in the gas and condensed phases in the range of saturation temperatures, which reduce the activity of the saturating phase and deteriorate the properties of the coatings, should be minimal.

The conceptual approach, which is the basis of the work, consists of the possibility of creating such conditions of chemical heat treatment (CHT), under which the saturation with silicon and boron will be determined by the partial pressure of their halides (chlorides, fluorides) and the phase composition of the coating by the phase composition of condensed substances. It should be noted that the physicochemical analysis of CHT processes does not provide an opportunity to evaluate the diffusion processes of coating formation, which occur due to the diffusion of saturating elements into the base.

Knowledge of the rational ratio of silicon powder, silicon and boron powders, and the activator, as well as the heating temperature of the metallizer and the processed materials, allows substantiating the choice of technological parameters of the process of saturation of alloys based on molybdenum with silicon, and silicon and boron.

Substances containing chlorine (for example, NH₄Cl, CCl₄, NiCl₂) or fluorine (for example, AlF₃, K₂SiF₆) can be used as activators [8,32]. At high temperatures, the activator decomposes with the release of chlorine (fluorine) or its compounds. The latter form with silicon (silicon and boron) halides (chlorides, fluorides) of different valence. The presence of silicon and boron halides ensures the flow of reverse chemical transport reactions. As a result, the delivery of saturating elements to the treated surface is realized.

The composition of some systems involving silicon, boron, and molybdenum, as well as the composition of the gas and condensed phases in the processing temperature range, are shown in Table 1.

From the analysis of the obtained results, it follows that the composition of the reaction medium, both gaseous and condensed phases, significantly depends on the composition of the system and the ratio of the starting reagents in it.

It was established that the introduction of silicon, chlorine, and molybdenum into the system's composition (system 1, Figure 2) is accompanied by the formation of silicon and molybdenum chlorides of different valences in the gas phase. At the same time, the partial pressure of SiCl₄ chloride is several orders of magnitude higher than that of SiCl₃, SiCl₂, SiCl, and molybdenum chlorides. Molybdenum chlorides MoCl₄ and MoCl₃ in the gas phase composition appear at a temperature of 1080 °C, which may indicate the flow of exchange reactions between chlorides and the matrix of the processed material in the reaction space. The formed molybdenum chlorides must participate in exchange reactions with silicon chlorides, contributing to the formation of active atoms of these elements, acceleration of adsorption, and diffusion processes. The latter should form a more developed diffusion zone. A transitional diffusion zone of considerable thickness contributes to the increase of adhesion of the coating to the base. Mo₅Si₃- and MoSi₂-type phases were found in the composition of the condensed phase.

№	Composition of the System, Mol	The Composition of the Environment	
		Gas Phase	Condensed Phase
1	Cl-Si-Mo = 0.5-1.0-0.5	SiCl ₄ , SiCl ₃ , SiCl ₂	Mo ₅ Si ₃ , MoSi ₂ , Mo
2	Cl-Si-B-Mo = 0.2-1.0-0.1-0.5	SiCl ₄ , SiCl ₃ , SiCl ₂ , BCl ₃ , BCl, SiCl, BCl, B ₂ Cl ₄ , MoCl ₃ , MoCl ₄	MoSi ₂ , MoB _{1.65} , MoB, MoB _{2.15} , Si, B
3	Cl-Si-B-Mo = 0.2-1.0-0.5-0.5	SiCl ₄ , SiCl ₃ , SiCl ₂ , BCl ₃ , BCl, SiCl, BCl, B ₂ Cl ₄ , MoCl ₃ , MoCl ₄	Si, MoSi ₂ , MoB _{2.15} , MoB _{1.65} , B, MoB _{3,8}
4	Cl-Si-B-Mo = 0.2-1.0-1.0-0.5	$\begin{array}{l} {\rm SiCl}_4, {\rm SiCl}_3, {\rm SiCl}_2, {\rm BCl}_3, {\rm BCl}, {\rm SiCl}, {\rm BCl}, \\ {\rm B}_2{\rm Cl}_4, {\rm MoCl}_3, {\rm MoCl}_4 \end{array}$	Si, MoSi ₂ , MoB _{2.15} , B, B_6 Si, MoB _{1.65} , MoB
5	Cl-Si-B-Mo-O = 0.2-1.0-1.0-0.5-0.1	BOC1, SiCl ₄ , SiCl ₃ , SiCl ₂ , BCl ₃ , BCl, SiCl, BCl, B ₂ Cl ₄ , MoCl ₃ , MoCl ₄	Si, MoSi ₂ , MoB _{2.15} , B, B ₆ Si, MoB _{1.65} ,MoB, SiO ₂
6	Cl-Si-B-Mo-O-N = 0.2-1.0-1.0-0.5-0.1-0.5	BOC1, SiCl ₄ , SiCl ₃ , SiCl ₂ , BCl ₃ , BCl, SiCl, BCl, B ₂ Cl ₄ , MoCl ₃ , N ₂ , MoCl ₄	BN, MoSi ₂ , MoB, Si ₂ N ₂ O
7	Cl-Si-B-Mo = 0.5-1.0-1.0-0.5	SiCl ₄ , SiCl ₃ , SiCl ₂ , BCl ₃ , BCl, SiCl, BCl, B ₂ Cl ₄ , MoCl ₃ , MoCl ₄	Si, MoSi ₂ , MoB _{2.15} , B, MoB _{1.65} , B ₆ Si, MoB
8	F-Si-B-Mo = 0.2-1.0-0.1-0.5	SiF_4 , BF_3 , SiF_2 , B_2F_4 , BF , SiF_3 , BF_2 , SiF	MoSi ₂ , MoB, Si
9	F-Si-B-Mo = 0.2-1.0-1.0-0.5	SiF ₄ , BF ₃ , SiF ₂ , B ₂ F ₄ , BF, SiF ₃ , BF ₂ , SiF	Si, MoSi ₂ , MoB _{2.15} , B, MoB _{1.65} , B ₆ Si, MoB

Table 1. Equilibrium composition of reaction media at temperatures of 298–1500 K and pressure in the system $P = 10^2 Pa$.



(a)

Figure 2. The equilibrium composition of system 1: Cl-Si-Mo = 0.5-1.0-0.5 mol: (a) gas phase; and (b) condensed phase.

The additional introduction of a small amount of boron into the system in the ratio Cl-Si-B-Mo = 0.2-1.0-0.1-0.5 (system 2, Figure 3) is accompanied by a slight decrease in the partial pressure of silicon chloride, SiCl₄, and the appearance of boron chlorides BCl₃, BCl, BCl₂, and B₂Cl₄, the partial pressure of which reaches high values.



Figure 3. The equilibrium composition of system 2: Cl-Si-B-Mo = 0.2-1.0-0.1-0.5 mol: (**a**) gas phase; and (**b**) condensed phase.

In the condensed state in systems containing boron, the Mo_5Si_3 phase disappears. The $MoSi_2$ phase stably exists in the entire studied temperature range and is approximately 0.45–0.40 kmol. In addition to the specified phases, the presence of compounds $MoB_{1.65}$, MoB, and $MoB_{2.15}$ is possible in the condensed state, but their amount is insignificant and does not exceed 0.05 kmol. According to literature data [33], $MoB_{2.15}$ diborides can either contain vacancies in the metal lattice or the corresponding compositions are mechanical mixtures of MB_2 with boron. The formation of solid solutions in systems $MB_{2.15}$ –boron is unlikely. On the contrary, for the "substoichiometric" borides, $MoB_{1.65}$, vacancies do not occur in the boron lattice, and these systems can be solid solutions of certain stoichiometric borides (or boron).

Increasing the amount of boron (systems 3 and 4, Figures 4 and 5) almost does not affect silicon and boron chlorides' composition and partial pressures. However, it affects the composition of the condensed phase. The MoSi₂ phase exists stably throughout the given temperature range, but its amount decreases and amounts to 0.3–0.22 kmol.

The decrease in the $MoSi_2$ phase can be explained by its partial dissociation. This process is observed with increasing temperature. The released silicon is released in the atomic state, which leads to an increase in its amount. Molybdenum interacts with boron to form the $MoB_{1.65}$ phase. The composition of the condensed phase is theoretically responsible for the phase composition of the coating. The obtained data on the composition of the condensed phase are consistent with the data of [10,11].

The presence of oxygen and nitrogen (the elements of the air) (systems 5 and 6, Figures 6 and 7) leads to the fact that, in the gas phase, there are chlorides of silicon, boron, and boron oxychloride, BOCl. Boron oxychloride has the maximum partial pressure. At the same time, the partial pressure of silicon chloride, SiCl₄, decreases.

At the same time, a small amount of silicon oxide, SiO_2 , appears in the condensed phase of systems containing oxygen. In systems containing nitrogen, molecular nitrogen, N₂, appears in the gas phase. Boron nitride, BN, molybdenum boride, MoB, and oxynitride, Si_2N_2O , observed in small quantities at 600 °C, also appear in the condensed phase. The formation of boron nitride can lead to embrittlement of the obtained coatings; however, the formation of a continuous layer based on BN should contribute to increasing the wear resistance of the coatings [34,35].





Figure 4. The equilibrium composition of system 3: Cl-Si-B-Mo = 0.2-1.0-0.5-0.5 mol: (**a**) gas phase; and (**b**) condensed phase.



Figure 5. The equilibrium composition of system 4: Cl-Si-B-Mo = 0.2-1.0-1.0-0.5 mol: (**a**) gas phase; and (**b**) condensed phase.

Silicon oxide, SiO₂, and oxynitride, Si₂N₂O, can occur in the reaction space during oxidation of the surface of the original silicon powder. The presence in the composition of condensed phases of oxides and oxynitrides in diffusion saturation is undesirable. These chemical compounds can be located between the crystallites of the phases formed in the diffusion saturation process. This can lead to a decrease in the operational properties of the coating [9].

That is why, when creating a method of applying complex boron–silicide coatings, one should provide for the possibility of removing excess oxygen from the reaction space, which can be achieved by pre-vacuuming the reaction chamber.



Figure 6. The equilibrium composition of system 5: Cl-Si-B-Mo-O = 0.2-1.0-1.0-0.5-0.1 mol: (**a**) gas phase; and (**b**) condensed phase.



Figure 7. The equilibrium composition of system 6: Cl-Si-B-Mo-O-N = 0.2-1.0-1.0-0.5-0.1-0.5 mol: (a) gas phase; and (b) condensed phase.

However, the formation of oxides and oxynitrides is advisable at the last stage of the process, as they will contribute to the formation of continuous protective films, which should contribute to increased heat resistance. According to the principle of continuity of Peeling-Bedwards [35], silicon forms a continuous protective film of SiO₂ (VsiO₂/Vsi = 1.9).

Increasing the amount of chlorine (system 7, Figure 8) does not affect the partial pressures of chlorides SiCl₃, SiCl₂, BCl₃, BCl, SiCl, BCl, and B₂Cl₄. However, it leads to a slight decrease in the partial pressure of silicon chloride, SiCl₄. Also, the temperature of the formation of the molybdenum chlorides MoCl₄ decreases to 920 °C, and, for MoCl₃, decreases to 1080 °C. The composition of the condensed phase does not change, but the amount of MoSi₂ decreases with increasing temperature and is 0.25–0.13 kmol. On the other hand, the amount of MoB_{2.15} increases and amounts to 0.25–0.20 kmol.



Figure 8. The equilibrium composition of system 7: Cl-Si-B-Mo = 0.5-1.0-1.0-0.5 mol: (**a**) gas phase; and (**b**) condensed phase.

The maximum values of the partial pressures of silicon and boron chlorides and the presence of molybdenum chlorides for all studied systems are observed in the temperature range of 1080–1250 °C. At the same time, the partial pressures of boron chlorides are inferior to the partial pressures of silicon chlorides. This may indicate that the thermodynamic probability of the boration process is lower than that of the siliconizing process.

Replacing chlorine with fluorine in the systems (systems 8 and 9, Figures 9 and 10) decreases the number of halides formed. Under these conditions, the formation of molybdenum fluorides is not observed. Molybdenum fluorides could participate in the exchange reaction flow between fluorides of saturating metals and the matrix. This process could provide the necessary degree of adhesion. The composition of the condensed phase does not change.



Figure 9. The equilibrium composition of system 8: F-Si-B-Mo = 0.2-1.0-0.1-0.5 mol: (**a**) gas phase; and (**b**) condensed phase.



Figure 10. The equilibrium composition of system 9: F-Si-B-Mo = 0.2-1.0-1.0-0.5 mol: (**a**) gas phase; and (**b**) condensed phase.

4. Discussion

Thus, theoretical calculations of the equilibrium composition of multicomponent systems with the participation of silicon, boron, molybdenum, nitrogen, oxygen, chlorine, and fluorine were carried out in the work. This provided an opportunity to determine the optimal technological parameters of the saturation process (temperature and reaction medium composition). The development of new rational methods of applying diffusion coatings with a high complex of properties is possible. The leading chemical reactions on the surface of molybdenum alloys under conditions of complex saturation with silicon and boron in a chlorine environment were determined. The data on the theoretical phase composition of coatings correlate well with the results of experimental studies presented in papers [10,36].

The nature of the change in the amount of condensed silicon is different from other condensed phases (Figures 4–6, 8 and 10). It is noted that, with increasing temperature, the content of condensed silicon gradually increases. The maximum value of silicon is recorded at a temperature of 900 °C, and, with a further increase in temperature, a decrease in its amount is noted. This dependence of the change in the amount of the condensed phase on the temperature change is determined by the chemical reactions that occur in the considered system. The superiority of one of the condensed phases over the others can be observed in the work [37]. Reducing the amount of excess phases in the condensed state is possible by reducing the amount of silicon in the initial parameters of the considered systems. A significant amount of silicon in the considered systems will not adversely affect the properties and characteristics of the coating.

5. Conclusions

Conducted theoretical studies of equilibrium systems with the participation of molybdenum, silicon, boron, fluorine, or chlorine in a specific temperature range made it possible to establish the influence of the composition of the initial components and the saturation temperature on the equilibrium composition of the gas and condensed phases.

The study of the gaseous and condensed states of Cl-Si-B-Mo and F-Si-B-Mo systems of different compositions in the temperature range of 200–1400 °C showed a significant probability of saturation of molybdenum-based alloys with such elements as silicon and boron.

It was found that the quantitative ratio of the system components does not affect the partial pressures of the silicon and boron halides formed. However, the use of chlorine-

containing activators is more expedient, as it leads to the formation of more chlorides of saturating elements (SiCl, SiCl₂, SiCl₃, SiCl₄, BCl, BCl₂, BCl₃, B₂Cl₄). As a result, the transfer of Si, B to the surface of saturating samples is facilitated. In addition, in chlorine-containing systems, molybdenum halides (MoCl₄, MoCl) are formed in the gas phase. This result may indicate the occurrence of exchange reactions between chlorides and matrix in the reaction space.

It was found that the ratio of the system components does not affect the composition of condensed phases, but does affect their quantitative ratio. By changing the ratio of silicon and boron, it is possible to obtain a coating of a given phase composition to meet necessary operational requirements.

When creating a method of complex saturation with silicon and boron, the possibility of removing excess oxygen from the reaction space should be provided. Thus, the formation of oxides among the condensed phases becomes unlikely.

It was determined that the temperature of 1100-1250 °C is rational for the saturation of molybdenum-based alloys with silicon and boron. A decrease in the temperature of the process is accompanied by a reduction in the partial pressures of the chlorides of the saturating elements and the absence of molybdenum chlorides, and its excess has practically no effect on the partial pressures of the chlorides.

The main chemical reactions taking place during the boron–siliconizing of molybdenum are defined, showing the possibility of simultaneous formation of molybdenum compounds with both silicon and boron. In this case, the most probable is the formation of MoSi₂, MoB, and MoB₂.

The analysis of the obtained data makes it possible to approach the development of new methods of complex saturation of molybdenum-based alloys with such chemical elements as silicon and boron correctly in the future.

Knowledge of the rational ratio of components and saturation temperature intervals makes it possible to justify the choice of technological parameters for the complex saturation of molybdenum-based alloys and obtain diffusion coatings of a predicted phase composition.

Theoretical calculations will significantly reduce the number of experiments in the future.

Further research will be aimed at the practical implementation of complex saturation of a molybdenum-based alloy with two chemical elements (silicon and boron). The quantitative composition of the saturating mixture and the process temperature will be determined based on the theoretical calculations performed in this work. In addition, in the future, experiments will be conducted to study the composition, microstructure, properties, and characteristics of borosilicate protective coatings of molybdenum-based alloys.

Author Contributions: Conceptualization, T.L., M.S., I.P. (Inna Pohrebova), Y.K. and M.B. (Maryna Bobina); methodology, T.L., M.S., V.I., I.P. (Inna Pohrebova), Y.K., M.B. (Maryna Bobina), N.K., M.B. (Marian Bartoszuk) and I.P. (Ivan Pavlenko); software, T.L., M.S., V.I., I.P. (Inna Pohrebova), Y.K., M.B. (Maryna Bobina), N.K., M.B. (Marian Bartoszuk) and I.P. (Ivan Pavlenko); validation, T.L., M.S., V.I., I.P. (Inna Pohrebova), Y.K., M.B. (Maryna Bobina), N.K., M.B. (Marian Bartoszuk) and I.P. (Ivan Pavlenko); formal analysis, T.L., M.S., V.I., I.P. (Inna Pohrebova), Y.K., M.B. (Maryna Bobina), N.K., M.B. (Marian Bartoszuk), I.P. (Ivan Pavlenko); investigation, T.L., M.S., V.I., I.P. (Inna Pohrebova), Y.K., M.B. (Maryna Bobina), N.K., M.B. (Marian Bartoszuk) and I.P. (Ivan Pavlenko); resources, T.L., M.S., V.I., I.P. (Inna Pohrebova), Y.K., M.B. (Maryna Bobina), N.K., M.B. (Marian Bartoszuk) and I.P. (Ivan Pavlenko); data curation, T.L., M.S., V.I., I.P. (Inna Pohrebova), Y.K., M.B. (Maryna Bobina), N.K., M.B. (Marian Bartoszuk) and I.P. (Ivan Pavlenko); writing-original draft preparation, T.L., M.S., I.P. (Inna Pohrebova), Y.K. and M.B. (Maryna Bobina); writing-review and editing, V.I., N.K., M.B. (Marian Bartoszuk), I.P. (Ivan Pavlenko); visualization, T.L., M.S., V.I., I.P. (Inna Pohrebova), Y.K., M.B. (Maryna Bobina), N.K., M.B. (Marian Bartoszuk) and I.P. (Ivan Pavlenko); supervision, T.L. and V.I.; project administration, V.I.; funding acquisition, V.I. All authors have read and agreed to the published version of the manuscript.

Funding: This work was partially supported by the International Association for Technological Development and Innovations (IATDI) and the International Innovation Foundation (IIF).

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The research was partially supported by the Research and Educational Center for Industrial Engineering (Sumy State University) and the Ministry of Education and Science of Ukraine (State Reg. No. 0122U200875).

Conflicts of Interest: The authors declare no conflicts of interest.

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