

# Thermodynamic modeling of composition and properties of self-fluxing materials based on the nickel

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**Abstract.** Self-fluxing nickel or cobalt-based alloys that use boron, phosphorus or silicon, as melting point depressants and fluxing agents are used as materials for applying thermal spray coatings. In this work, thermodynamic simulation of self-fluxing materials Ni-0.5C-15Cr-3.2Si-2B (PGSR-2) and Ni-1C-17Cr-4.1Si-3.6B (PGSR-4) was performed. As the software for simulation of phase and chemical equilibrium the TERRA software package was used. The simulation was carried out in the temperature range 300–3000 K at a total pressure  $P = 10^5$  Pa in an argon atmosphere. The temperature dependences of the equilibrium composition and thermodynamic characteristics (enthalpy, entropy, and Gibbs energy) of the alloys of the investigated systems were calculated. It is shown that Ni, Cr, C, Ni<sub>3</sub>B, Ni<sub>2</sub>B, NiB, Ni<sub>2</sub>Si, NiSi, CrB, CrSi can be formed in the condensed phase under equilibrium heating of PGSR-2. When PGSR-4 is heated in the condensed phase, along with the above components, Cr<sub>3</sub>B<sub>3</sub>, CrB<sub>2</sub>, and Cr<sub>3</sub>C<sub>2</sub> compounds can be formed. The temperature dependences of the thermodynamic characteristics of the systems studied have kinks that can be explained by phase transformations.

## 1 Introduction

One of the promising directions in the development of modern materials science is the application of gas-thermal coatings that can increase the durability of parts and machines when working at high temperatures and abrasive wear [1-4].

Among the wide variety of powder materials used for applying gas-thermal coatings, self-fluxing alloys are used [5-6]. The most important factors that ensure the manufacturability of self-fluxing alloys are the low melting point, high wettability, and proximity of the thermal characteristics of the main and deposited materials [7].

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The performance characteristics of coatings based on self-fluxing alloys are determined by the following factors [8]: the type of base of the self-fluxing alloy, the volume fraction and stoichiometry of the hardening phase, and the method of coating formation.

Currently, nickel or cobalt-based alloys have been developed that use boron, phosphorus, or silicon, individually or in combination, as melting point depressants and fluxing agents [6-9]. So, silicon and boron present in the alloys reduce their melting point by several hundred degrees and protect the surface layers from oxidation.

The processability of Ni-Cr-Si-B alloys is explained by the formation of a heterogeneous eutectic structure with its characteristic low melting point (about 1000°C) [9]. Therefore, these materials are widely used for surface hardening and restoration of the geometry of machine parts operating under conditions of abrasive wear, under the influence of high temperatures and aggressive environments. In addition, self-fluxing nickel alloys are widely used as matrix materials that form the basis of composite coatings.

Tribological properties of self-fluxing materials are largely determined by the content of strengthening compounds in the alloy matrix. The chemical composition, stoichiometry, and volume fraction of these compounds in alloys depend on the amount of chromium, boron, carbon, and silicon. The list of strengthening compounds formed during the formation of coatings of the Ni-Cr-Si-B system using various technologies, as well as their structural type and some properties are given in [8, 10-11]. It is indicated that the following types of strengthening compounds can be formed: carbides ( $Me_7C_3$ ,  $Me_3C_2$ ,  $Me_{23}C_6$ ), borides ( $MeB$ ,  $Me_5B_3$ ,  $Ni_3B$ ) and carboborides ( $Me_3(C, B)$ ,  $Me_{23}(C, B)$ ) of various stoichiometry (Me – Cr, Fe).

Coatings formed during surfacing of these powders have high hardness and wear resistance due to the formation of fine particles of strengthening phases, such as CrB,  $Cr_{23}C_6$ ,  $Cr_7C_3$ , etc. [12]. Additional alloying with refractory metals of the second subgroup of the Periodic system of elements (Hf, V, Ti, Mo, Zr, Nb, and so on) leads to the grinding of the structure and the formation of wear-resistant refractory particles based on them.

One of the most technologically advanced methods of applying protective coatings made of self-fluxing alloys is plasma spraying [1-4]. The melting of the surface layers obtained in this way makes it possible to reduce the degree of material defects and increase the strength of the coatings' connection with the base metal. Another method of applying self-fluxing coatings is laser surfacing, the advantages of which are related to the high power density of laser installations and the short duration of high-temperature exposure [12].

To design and optimize the processes of applying gas-thermal coatings, it is necessary to improve our understanding of the structure of liquid alloys, since heat treatment of the melt can strongly affect the properties of solidified materials [13-15]. The composition, structure, and content of components, and, consequently, the integral physical and chemical properties of new materials, depend on the initial ratio of elements, parameters, and the degree of non-equilibrium of the system under study (heating and cooling rates, temperature gradients, and other technological factors). When implementing a stable controlled process, it is often necessary to vary the input parameters: initial composition, temperature, pressure, etc. The selection of these parameters can be carried out to a large extent by means of thermodynamic calculations, which can significantly reduce the volume of experimental studies and, thereby, reduce time and material costs. For equilibrium (quasi-equilibrium) processes, thermodynamic calculations are a necessary stage of research. In the case of non-equilibrium processes, thermodynamic calculations allow us to estimate the limit values of various process parameters.

The aim of this work is to study the equilibrium composition and thermodynamic characteristics of self-fluxing alloys Ni-0.5 C-15Cr-3.2 Si-2B and Ni-1C-17Cr-4.1 Si-3.6 B in a wide temperature range.

## 2 Method of investigation

The computer experiment was performed using the thermodynamic modeling technique. The TERRA software package was used as software for modeling phase and chemical equilibrium [16-19].

The thermodynamic equilibrium model is widely used in scientific and industrial practice when studying the behavior of complex chemical systems at elevated temperatures, when chemical or phase transformations have a significant role. In chemical and technological processes, the main task of modeling is to determine the composition of phase components. In power engineering, heat engineering, and plasma chemistry, it is also necessary to find the properties of the system, such as enthalpy, specific heat, and transfer coefficients. The assumption of phase and chemical equilibrium for real processes serves as a limiting estimate of states, but even this information has an invaluable role in the analysis of poorly studied systems.

Calculation of the thermodynamic equilibrium of arbitrary multicomponent systems consists in determining all the equilibrium parameters, thermodynamic properties, and chemical and phase composition. At a sufficiently high temperature, when any changes in the state are accompanied by phase, polymorphic, and chemical transformations, this problem is immeasurably more complex than in the formulation of classical thermodynamics. However, due to the fact that the fundamental thermodynamic laws remain valid for all systems, their correct application allows us to solve the problem of calculating thermodynamic equilibrium in the general case.

The advantage of the thermodynamic method lies in its universal nature, which allows us to study systems of arbitrary chemical composition based only on reference information about the thermochemical and thermodynamic properties of individual substances – components of equilibrium. These properties are known for a wide range of chemical compounds that are in a gaseous, condensed, and ionized state, in the temperature range typical for most engineering applications. However, the physical transparency of the thermodynamic transition to modeling is combined with the computational complexity of the generalized algorithm, the difficulties of preparing initial data and presenting a set of results.

## 3 Results and discussion

The simulation was carried out in the temperature range 300 – 4000 K at a total pressure of  $P = 10^5$  Pa in the argon atmosphere. The initial compositions of the simulated systems corresponded to the compositions of nickel-based self-fluxing powder materials (mass. %):

- 1) Ni - 79.3, C - 0.5, Cr - 15, Si - 3.2, B - 2 (PGSR-2);
- 2) Ni - 74.3, C - 1, Cr - 17, Si - 4.1, B - 3.6 (PGSR-4).

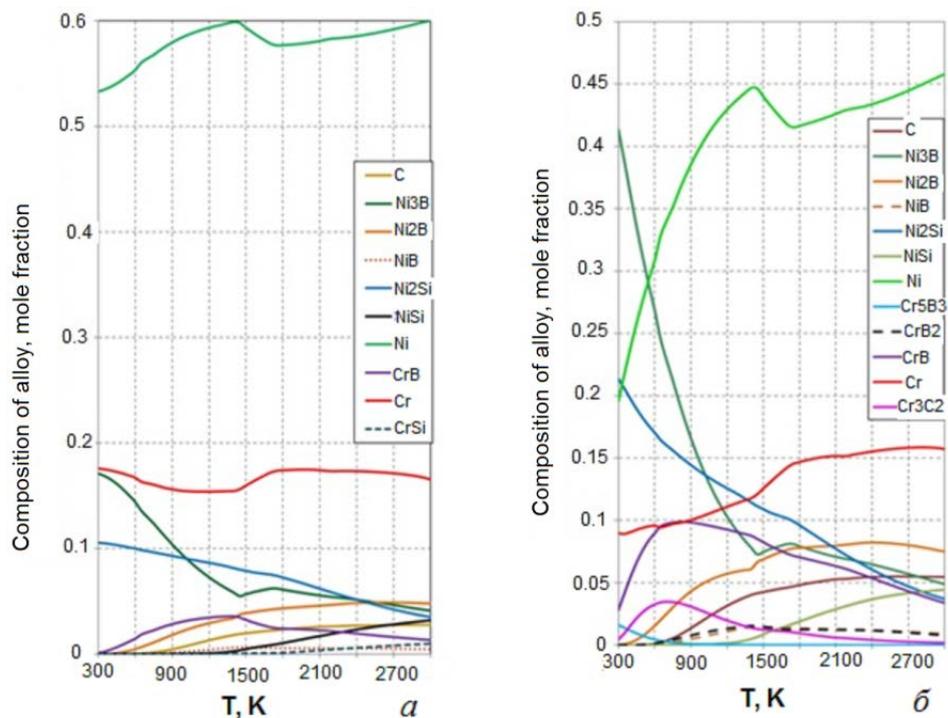
The argon content for both simulated systems was 1 mass. %.

The following elements, ions, and compounds were taken into account in the simulation: gaseous Ar, electronic gas e-, Ni, C, Cr, Si, B, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, Si<sub>2</sub>, Si<sub>3</sub>, SiC, Si<sub>2</sub>C, SiC<sub>2</sub>, Si<sub>2</sub>C<sub>2</sub>, Si<sub>3</sub>C, B<sub>2</sub>, BC, B<sub>2</sub>C, BC<sub>2</sub>, Cr<sub>2</sub>, CrC<sub>2</sub>, Ar<sup>+</sup>, Si<sup>+</sup>, Ni<sup>+</sup>, Cr<sup>+</sup>, B<sup>+</sup>, C<sup>+</sup>, C<sup>-</sup>, C<sub>2</sub><sup>+</sup>, C<sub>2</sub><sup>-</sup>; condensed Ni, C, Cr, Si, B, Ni<sub>3</sub>C, NiB, Ni<sub>3</sub>B, Ni<sub>2</sub>B, Ni<sub>4</sub>B<sub>3</sub>, NiSi, NiSi<sub>2</sub>, Ni<sub>2</sub>Si, Ni<sub>7</sub>Si<sub>13</sub>, SiC, SiB<sub>14</sub>, B<sub>4</sub>Si, B<sub>6</sub>Si, B<sub>4</sub>C, CrB, CrB<sub>2</sub>, Cr<sub>3</sub>B<sub>4</sub>, Cr<sub>5</sub>B<sub>3</sub>, Cr<sub>3</sub>C<sub>2</sub>, Cr<sub>7</sub>C<sub>3</sub>, Cr<sub>23</sub>C<sub>6</sub>, CrSi, CrSi<sub>2</sub>, Cr<sub>3</sub>Si, Cr<sub>5</sub>Si<sub>3</sub>.

Information about the properties of some components was taken from the TERRA.props database and from the literature [20-24]. However, it should be noted that in the available literature, information about the thermodynamic properties of a number of binary compounds in the condensed state (solid and liquid) is absent, and sometimes contradictory. Therefore, thermodynamic properties (standard enthalpy and entropy of formation,

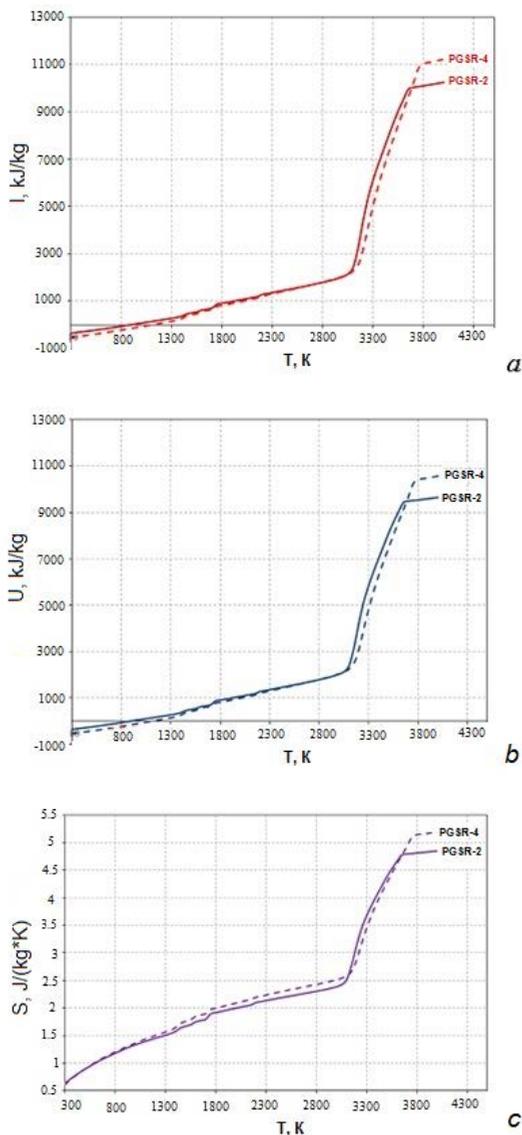
temperature dependences of heat capacities) were calculated using various calculation methods (see, for example, [25-27]).

Fig.1 shows the temperature dependences of the content of components of the condensed phase formed during equilibrium heating of PGSR-2 (a) and PGSR-4 (b) alloys. As can be seen from Fig.1-a, in the condensed phase formed during heating of PGSR-2, the existence of Ni, Cr, C, Ni<sub>3</sub>B, Ni<sub>2</sub>B, NiB, Ni<sub>2</sub>Si, NiSi, CrB, CrSi is possible. Fig.1-b shows that when the PGSP-4 alloy is heated in the condensed phase, along with the above components, Cr<sub>5</sub>B<sub>3</sub>, CrB<sub>2</sub>, Cr<sub>3</sub>C<sub>2</sub> compounds are also formed. The content of other components is insignificant (less than 1 mass. %).



**Fig. 1.** Temperature dependences of the content of components of the condensed phase formed during equilibrium heating of PGSR-2 (a) and PGSR-4 (b) alloys.

Fig.2 shows the temperature dependences of the enthalpy, internal energy and entropy of PGSR-2 and PGSR-4 alloys. As can be seen from Fig.2, the values of all these characteristics increase nonmonotonically as the temperature increases. When analyzing and comparing the temperature dependences of the content of the condensed phase components (Fig.1) with the temperature dependences of the thermodynamic characteristics of the systems under study (Fig.2), it is clear that there is a correlation between them: breaks in the dependences are observed at the same temperatures. These changes can be explained by phase transitions that occur in the system.



**Fig. 2.** Temperature dependences of enthalpy (a), internal energy (b), and entropy (c) of PGSR-2 and PGSR-4 alloys.

## 4 Conclusion

Thermodynamic modeling of the equilibrium composition and thermodynamic characteristics of self-fluxing nickel-based alloys Ni-0.5 C-15Cr-3.2 Si-2B (PGSR-2) and Ni-1C-17Cr-4.1 Si-3.6 B (PGSR-4) is performed. The simulation results show that Ni, Cr, C, Ni<sub>3</sub>B, Ni<sub>2</sub>B, NiB, Ni<sub>2</sub>Si, NiSi, CrB, CrSi can be formed in the condensed phase under equilibrium heating of PGSR-2 and PGSR-4. In addition, when PGSR-4 is heated in the condensed phase, along with the above components, Cr<sub>5</sub>B<sub>3</sub>, CrB<sub>2</sub>, and Cr<sub>3</sub>C<sub>2</sub> compounds can be formed. It is shown that the temperature dependences of the thermodynamic parameters (enthalpy, internal energy and entropy) are non-monotonous. There are sharp

breaks on the curves of  $I=I(T)$ ,  $S=S(T)$ , and  $U=U(T)$  at temperatures corresponding to the phase transformations occurring in the systems under study.

Thus, we can conclude that the results obtained allow us to estimate the composition of the condensed phase formed during equilibrium heating of the systems under study, and to predict the behavior of materials under extreme conditions.

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