Thermodynamic modeling of Ni-Cr-B-C-Si system in "air+propane" atmosphere

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Abstract. In this paper, thermodynamic modeling of a powder self-fluxing material PGSR-2 based on nickel (wt. %): Ni-79.3, C-0.5, Cr-15, Si-3.2, B-2 was carried out. The simulation was performed in the temperature range of 300-6000 K in the atmosphere of "92 vol. % air + 8 vol. % propane" at a total pressure of P=10^5 Pa. The temperature dependences of the equilibrium composition of the condensed and gas phases formed during heating are calculated.

The development of protective gas-thermal coatings, the complex of mechanical properties of which will increase the durability of parts when working in conditions of high temperatures and abrasive wear, is a promising direction in the development of modern materials science.

Nowadays among the used gas-thermal coating methods the most widespread is plasma powder spraying, which provides a wide range of coating properties, high performance and versatility. For the application of gas-thermal coatings, various powder materials are used, including self-fluxing alloys [1–6]. The main feature of these materials is the presence of fluxing components (Si, B, less often Mn) in their compositions, which protect the coatings from the oxidative processes during surfacing. The most important factors that ensure the manufacturability of self-fluxing alloys are the low melting point, high wettability, and the proximity of the thermophysical characteristics of the base and surfaced materials. The most common materials used for surface hardening of parts are self-fluxing alloys of the Ni-Cr-Si-B system.

The properties of plasma coatings significantly depend on the parameters of plasma deposition (current, arc voltage, technological parameters of the plasma torch, chemical composition of the plasma-forming gas and the sprayed material, their mass flow rate, etc.).

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 the heat treatment of the melt can greatly affect the properties of solidified materials [7].

One of the most effective ways to solve this problem is the use of thermodynamic modeling methods, which allow us to obtain the maximum amount of information about the process under study with a minimum of expensive experimental investigations.

The thermodynamic equilibrium model is widely used in scientific and industrial practice in the study of the behavior of complex chemical composition systems at high 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 the components of the phases. In power engineering, heat engineering, and plasma chemistry, it is also necessary to find the properties of the
system, such as enthalpy, specific heat capacity, and transfer coefficients. The assumption of phase and chemical equilibrium for real processes undoubtedly serves as a limiting estimate of states, but even such information plays an invaluable role in the analysis of poorly studied systems.

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

The simulation was performed in the temperature range of 300-6000 K at a total pressure of P=10^5 Pa. A mixture of 92 vol.% air + 8 vol.% propane was considered as a plasma-forming gas. The initial composition of the simulated system corresponded to the composition of the powder self-fluxing material PGSR-2 based on nickel (wt.%): Ni-79.3, C-0.5, Cr-15, Si-3.2, B-2. When preparing the initial data for modeling, the technological parameters of the installation were taken into account: the flow rate of plasma-forming gas - 1 l/s, the flow rate of powder -1 g/s.

As the software the system for modeling phase and chemical equilibria "TERRA" developed at the Bauman Moscow State Technical University (Moscow) [8-10] was used.

Figure 1 shows the temperature dependences of the content of the components of the condensed phase formed during the equilibrium heating of PGSR-2 in the atmosphere of the plasma-forming gas.

![Figure 1](image_url)

**Figure 1.** Temperature dependences of the content of the components of the condensed phase formed during the equilibrium heating of the PGSR2 system in the atmosphere 92 vol.% air + 8 vol.% propane.

As can be seen from this figure, the existence of Ni, Cr, C, Na2O, B2O3, BN, Cr2O3, ZrO2, HFO2, Cr7C3, Cr3C2 is possible in the condensed phase. The content of other components is insignificant (less than 0.01 wt.%). The nickel content is constant in the temperature range of 300-2300 K. The decrease in the mass fraction of nickel at T=1900 K is due to the formation of the Ni2Si compound, which exists in a narrow temperature range of 1900-2000 K. Chromium oxide Cr2O3 is stable in the temperature range of 300-1400 K. With a further increase in temperature, the content of Cr2O3 decreases, while in the temperature range of 1300-1500 K, the formation of chromium carbide Cr3C2 is observed, and in the temperature range of 1500-1900 K – chromium carbide Cr7C3.

At T ≥ 1800 K the content of Cr7C3 decreases sharply, and at 1900 – 2400 K, the appearance of chromium in the condensed phase is observed. Silicon oxide SiO2 in the condensed phase exists in the temperature range of 300-2100 K, and, in the temperature range of 300-1800 K, the SiO2 content is unchanged. Besides that, SiO2, B2O3, and C can be formed in the condensed phase. The content of these components is less than 0.05 wt.%. 

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Figure 2 shows the temperature dependences of the partial pressures of the components of the gas phase formed during the equilibrium heating of the PGSR2 system in the atmosphere of air + propane.

![Figure 2](image)

**Figure 2.** Temperature dependences of the partial pressures of the components of the gas phase formed during the equilibrium heating of the PGSR2 system in the atmosphere 92 vol.% air + 8 vol.% propane.

In our investigation the partial pressures of the components not lower than $10^{-6}$ MPa (1 Pa) were taken into account. The main components of the gas phase in the entire studied temperature range are N$_2$, H$_2$, CO, H$_2$O, and CO$_2$. The partial pressures of H$_2$, CO, H$_2$O, and CO$_2$ change nonmonotonically with increasing of temperature, and the pressure of N$_2$ decreases monotonically. The contribution of the remaining components of the gas phase to the total pressure becomes noticeable at $T \geq 1300$ K. It should be noted that in the studied temperature range, the main ionized components of the gas phase are the electron gas e$^-$, as well as the Ni$^+$ and Cr$^+$ ions.

Thus, the results obtained allow us to estimate the composition of the condensed and gas phases formed during the equilibrium heating of the studied system, and to predict the behavior of materials under extreme conditions. It should be noted that the methods and calculation algorithms used by us are designed to simulate extremely equilibrium states of complex systems and do not allow us to find the "trajectory" of the transition to the equilibrium state.

**Acknowledgments**
The reported study was funded by RFBR, project number №20-21-00063 Rosatom.

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