Thermodynamic aspects of electron-beam surface modification of low-carbon steel

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Abstract. Multicomponent surface modification of carbon steels is of high interest in mechanical engineering due to its beneficial impact on machine components' and structures' surface properties. The present research was devoted to simulating the process of aluminides and borides formation on the surface of low-carbon steel during electron beam alloying and predict the phase composition of the obtained coatings. Computational thermodynamics and approximate calculation method were used to solve the problem mentioned above. Calculations were done in the temperature range between 200 and 2000 K at 10⁻³ Pa. It was discovered that the calculated and experimental data of the coating's phase composition differs significantly. The only confirmed phase that was predicted by the calculations was sodium fluoride (NaF). It was established that NaF presence in the treatment paste was redundant for the electron beam alloying because of its low reactivity in a vacuum. XRD analysis revealed the following phases in the coating: Fe₂B, Fe₃C, and AlFe₃.

1. Introduction
Electron-beam processing (EBP) as a method of surface modification is continuously studied and is on high demand due to its application perspectives [1-3]. It can be used to achieve protective coatings on the surface of steels and alloys in two ways: electron beam alloying (EBA) and combined treatment. The latter process comprises two stages:
- thermal-chemical surface treatment (TCT) as a first step, where diffusion layers are formed on the surface of the base metal during high-temperature exposure in treatment media in a muffle furnace [4-6];
- the second step involves modification of the obtained diffusion layers using EBP.

In both EBA and combined treatment (TCT+EBP), varying the composition or ratio of the treatment mixture components allows obtaining specific structure formation of the layers and their desired properties. For instance, surface treatment of steels and alloys with boron and aluminum results in layers with increased oxidation and wear resistance [7]. For the muffle furnace's diffusion process, the optimal ratio of B₃C: Al in treatment paste was experimentally revealed as 5:1.
Thermodynamic calculations for TCT processes as boriding and boroaluminizing are presented in papers [8,9]. In both articles, the software was used to calculate thermodynamics. Another way to predict phase composition and the probability of chemical reactions under certain conditions can be determined by Gibbs energy calculations (approximate calculation method). The chemical reactions for boroaluminizing in the furnace without a protective atmosphere are given in paper [10].

The purpose of this study is to come up with a model of synthesis of iron borides and aluminides on the surface of low-carbon steel using EBA in a vacuum. Simulation is planned to implement in two ways: using TERRA software and by approximate calculation method. These methods will be discussed more carefully below. It is also aimed to support calculations by experimental data.

2. Thermodynamic modeling

Computational thermodynamics was carried out TERRA software. The program is designed to calculate systems of arbitrary character with chemical and phase transformations. It enables the simulation of an extremely equilibrium state by implementing the method and calculation algorithm developed at Bauman Moscow State Technical University [11]. The program is linked to an extensive database of various substances' properties, making it suitable for studying compositions with arbitrary chemical composition. The study examined the reactions in the coating under the influence of an intense electron beam in a vacuum. The paste composition was taken from the atomic masses of its component substances (table 1).

### Table 1. Input composition of the paste in atomic mass for calculations

| Paste components | B₄C | Al | NaF |
|------------------|-----|----|-----|
| Atomic mass      | 56  | 27 | 42  |

First, reactions occurring in the coating at a temperature between range 200 and 2000 K at 10⁻³ Pa were simulated. Figure 1 shows the appearance of aluminum diboride (AlB₂), which can play a significant role in forming iron borides and aluminides. The possible rest phases were C, Na, and Na₃AlF₆.

![Figure 1](image-url)  
**Figure 1.** The output of the condensed phases in the treatment paste (T=200-2000K, P=10⁻³Pa)
Then, the reactions between the coating and steel substrate were simulated. Low-carbon steel was used in the current research, so we neglected the steel's carbon content and other elements, except for the iron. Table 2 presents the composition of the paste and iron in the atomic masses.

Table 2. Input composition of the paste and iron in atomic mass for calculations

| Paste components | Fe | B\textsubscript{4}C | Al | NaF |
|------------------|----|----------------|----|-----|
| Atomic mass      | 56 | 56             | 27 | 42  |

Figure 2 shows the output of the condensed phases during the synthesis of transition metal borides in St3 steel (T=250-2000 K, P=10\textsuperscript{-3} Pa). Calculations showed that iron boride FeB appeared in addition to the phases mentioned above.

Approximate calculation method. The probability of chemical reactions was determined by the approximate calculation method. The calculation of the chemical reaction equilibrium is estimative, allowing to assess a reaction's potential at a given temperature. Table 3 presents the approximate $\Delta G$ values for the following reactions:

\begin{align*}
\text{NaF} + \text{B} & \rightarrow \text{Na} + \text{BF} \\
3\text{NaF} + \text{Al} & \rightarrow 3\text{Na} + \text{AlF}_3 \\
3\text{NaF} + \text{AlF}_3 & \rightarrow \text{Na}_3\text{AlF}_6 \\
2\text{B} + \text{Al} & \rightarrow \text{AlB}_2 \\
\text{B}_4\text{C} + 2\text{Al} & \rightarrow 2\text{AlB}_2 + \text{C} \\
2\text{Fe} + 3\text{B}_4\text{C} + 2\text{Al} + 6\text{NaF} & \rightarrow 2\text{FeB} + 2\text{AlB}_2 + \text{Na}_3\text{AlF}_6 + 3\text{Na} + \text{C}
\end{align*}
Table 3. Approximate values ΔG (kJ mol⁻¹)

| T, [K] | Reaction 1 | Reaction 2 | Reaction 3 | Reaction 4 | Reaction 5 | Reaction 6 |
|--------|------------|------------|------------|------------|------------|------------|
| 298.15 | 416.64     | 207.9      | -87.63     | -149.38    | -237.43    | -2923.51   |
| 400    | 394.34     | 195.7      | -89.09     | -148.42    | -235.56    | -2937.65   |
| 600    | 356.34     | 184.2      | -91.99     | -146.08    | -231.11    | -2950.75   |
| 800    | 320.3      | 173.74     | -96.22     | -143.26    | -226.72    | -2961.83   |
| 1000   | 286.08     | 179.13     | -111.57    | -128.65    | -199.8     | -2952.55   |
| 1200   | 256.04     | 185.45     | -117.02    | -123.79    | -193.05    | -2944.37   |
| 1400   | 261.06     | 294.74     | -142.46    | -129.99    | -208.65    | -2857.04   |
| 1600   | 236.78     | 314.16     | -167.07    | -138.17    | -227.98    | -2866.62   |
| 1800   | 212.77     | 332.5      | -193.14    | -151.3     | -256.53    | -2879.47   |
| 2000   | 188.71     | 348.94     | -220.44    | -169.62    | -294.45    | -2869.15   |

Approximate calculations was carried out according to the sequence reported in [10]. Standard enthalpy for ΔH²⁹⁸ substances formation and standard ΔS²⁹⁸ entropy were found in reference sources [12-13]. The formulas (Eq. 7) and (Eq. 8) determined the change in enthalpy ΔHᵣ for and entropy ΔSᵣ as a result of the reaction, and then, using formula (Eq. 9), the change in free energy ΔGᵣ at temperature T was calculated, as follows:

\[ \Delta H_r^0 = \sum_{products} \Delta H_r^0 - \sum_{reactants} \Delta H_r^0 \]  \hspace{1cm} (7)
\[ \Delta S_r^0 = \sum_{products} \Delta S_r^0 - \sum_{reactants} \Delta S_r^0 \]  \hspace{1cm} (8)
\[ \Delta G_r^0 = \Delta H_r^0 - T \]  \hspace{1cm} (9)

The calculation showed that the last reaction (Eq. 6) is the most probable, considering its high thermodynamic potential.

3. Methodology of Experiment

Low-carbon St3 steel (0.2% C) was used as a test material (analog to A284Gr.D steel). It is used to produce profiled bars and bar irons, sheet and plate steel, cold-rolled, and broadband sheet products. Moreover, this steel is a foundation for pipes (including rectangular pipes), forgings and stampings, tapes, metalware, and wires.

The treatment mixture composition was taken as B₄C -78%, Al-18%, and NaF-4% (wt.) and ethyl alcohol as a binder [10]. The obtained paste was applied to the samples’ defatted surface using a brush with a uniform layer of 0.5-1 mm.

Electronic heating with a continuous beam was carried out for 1-3 minutes at a specific power of W=5.7×10² W/mm² (diameter of the electron beam d=1 mm). The residual pressure in the vacuum chamber did not exceed 2×10⁻³ Pa.

XRD analysis was carried out on a Phaser 2D Bruker diffractometer (Cu Kα - radiation). Microhardness was measured on a PMT-3M microhardness tester. The microhardness tester is equipped with an adapter with a digital camera and the NEXSYS ImageExpert MicroHardness 2 fingerprint image processing program (Russian State Standard 9450-76).

Cross-sections of the samples’ microstructure was studied using a METAM RV-21 metallographic microscope equipped with a VEC-335 digital camera and the NEXSYS Image Expert Pro 3.0 software package for quantitative metallographic analysis.
4. Results

The layer with the thickness of 240-260 μm was obtained as a result of EBA (figure 3). The microstructure of the layer consisted of the light zone with embedded dark dendrites. Underneath the layer carbon-rich zone in the form of perlite was obtained due to carbon displacement from the surface by alloying elements. XRD analysis showed the presence of Fe₂B, Fe₃C, AlFe₃, and NaF. The last phase is the only one compound that was predicted by calculations. However, it is known that iron borides and aluminides form during the boroaluminizing process or alloying from boron/aluminum-containing powders. The formation of cementite seems to be reasonable due to the boron carbide presence in the treatment paste.

The microhardness measurements showed that the coating hardness was twice as higher as the substrate hardness (figure 3). The maximum value in the coating reached 3800 MPa at around 100 μm from the surface. Just below the coating, the second rise of the hardness was visible in the perlite-rich zone. The relatively low microhardness of the layer was probably due to the low concentration of iron boride.

Based on the experimental results additional chemical reactions were possible in the thermodynamic system:

\[
14\text{Fe} + B_4\text{C} + \text{Al} + \text{NaF} \rightarrow 4\text{Fe}_2\text{B} + \text{Fe}_3\text{C} + \text{AlFe}_3 + \text{NaF} \quad (10)
\]
\[
14\text{Fe} + B_4\text{C} + \text{Al} \rightarrow 4\text{Fe}_2\text{B} + \text{Fe}_3\text{C} + \text{AlFe}_3 \quad (11)
\]
\[
B_4\text{C} + 11\text{Fe} \rightarrow 4\text{Fe}_2\text{B} + \text{Fe}_3\text{C} \quad (12)
\]

| T, [K] | Reaction 10 | Reaction 11 | Reaction 12 |
|--------|-------------|-------------|-------------|
| 1600   | 71.12       | -619.2      | -362.25     |

Table 4. Approximate values \(\Delta G\) (kJ·mol\(^{-1}\))

Figure 3. The microstructure and microhardness distribution of St3 steel after EBA
Figure 4. The XRD pattern of St3 steel after EBA

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Conclusion
The presence of activator (NaF) in the treatment paste is redundant for the EBP in a vacuum because XRD analysis has shown its traces after EBA. Besides, the calculation of reactions with sodium fluoride has shown their low probability (positive Gibbs energy), except for the reactions with Na$_3$AlF$_6$. However, the latter one wasn't confirmed by XRD analysis.

The interaction of B$_4$C+Al+NaF reaction mixture with the St3 steel surface in the temperature range from 250 to 2000 K has shown that the predicted coating’s phase composition and experimental data differs significantly. Calculation methodology needs to be improved to provide adequate prediction functions. One of the reliable approaches is to utilize verified thermodynamic databases.

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