Calculated substantiation of isolation of boron and sodium cations from molten working and heating medium during hardening of restored parts

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Abstract. Scientific and technological research in the development of the technical process for the restoration and strengthening of worn parts using calculated justification allowed us to make an optimal technical decision on the development of a method for surfacing and electrolysis borating of parts to increase their service life. The working medium for strengthening the restored tillage organs of agricultural aggregates is substantiated theoretically using the developed mathematical model describing the working medium as a thermodynamic system consisting of boron cations, sodium and oxygen anions. The creation of a potential difference in this medium will provide a process in which boron and sodium ions are discharged at the cathode, and oxygen ions at the anode. For this, it is necessary to theoretically determine the electromotive forces of polarization of electrolytic cells and compare them. The solution to this problem requires an assessment of the change in the Gibbs energy during the decomposition of sodium oxide and boric anhydride for the temperature of the borating process, taking into account its change under standard conditions, the chemical potentials of the reacting components and phase transitions, the melting of substances and their sublimation. The order in which boron and sodium are separated at the cathode is determined by comparing the electromotive forces of polarization of boric anhydride and sodium oxide. It was found that sodium oxide is more stable than boric anhydride. Consequently, boron atoms are reduced on the cathode surface, and calculations have confirmed the possibility of its use.

1. Introduction
The adoption of an optimal technical solution in the development of a technological process for the restoration and hardening of worn parts requires its computational verification. As a result of scientific and technological research, methods were developed for surfacing and electrolysis borating of these parts to increase their technical resource [1, 2, 4, 11].

The possibility of using the developed composition as a working and heating medium for strengthening the restored tillage organs of agricultural aggregates must be established theoretically [11]. This requires a mathematical model describing the working and heating medium as a thermodynamic system.

The molten working and heating medium is thermodynamically considered as a system consisting of boron, sodium and oxygen anions [1, 6, 8, 7]. The creation of a potential difference in the molten working and heating medium will provide a process in which boron and sodium ions are discharged at
the cathode, and oxygen ions at the anode.

2. The object and method of research
For a quantitative assessment of the sequence of isolation of sodium and boron from the developed borate-sodium melt [10], it is necessary to theoretically determine electromotive forces of polarization of electrolytic cells and compare them.

In electrolytic cells, decomposition reactions of sodium oxide and boric anhydride take place.

The change in the Gibbs energy during the decomposition of sodium oxide is determined for the temperature of the borating process, taking into account the change in this energy under standard conditions, as well as the chemical potentials of the reacting components [3, 5, 6, 10]. It is also necessary to consider phase transitions, melting of substances and their sublimation. Therefore, this change is determined taking into account the Van't Hoff equation as follows:

$$
\Delta G_{1,T} = \Delta G_{1,T}^0 + R_T \ln \left( \frac{p_{O_2}}{p_{O_2}^0} \right) \cdot \left( \alpha_1 \right)^{-1},
$$

(1)

where

$$
\Delta G_{1,T}^0 = \Delta G_{1,T}^0 - T \cdot \Delta S_{1,T}^0 - \Delta H_{1,T}^0,
$$

(2)

where $T$ – the process temperature, ºС; $R_T$ – the universal gas constant, J/K·mol; $p_{O_2}$ – the partial pressure of oxygen, Pa; $\alpha_1$ – the activity of sodium oxide:

$$
\Delta H_{1,T}^0 = \Delta H_{1,T}^0 - T \cdot \Delta S_{1,T}^0 - \Delta H_{1,T}^0.
$$

The change in the Gibbs energy of the decomposition reaction of sodium oxide at operating temperature is determined by the formula (3):

$$
\Delta f_{1,T}^0 = \Delta f_{1,T}^0 + \int_{T_0}^{T} C_i^T dT \cdot \Delta H_{1,T}^0,
$$

(3)

where

$$
\Delta S_{1,T}^0 = \Delta S_{1,T}^0 + \int_{T_0}^{T} C_i^T dT \cdot \Delta H_{1,T}^0.
$$

(4)

The electromotive force of polarization is calculated, taking into account the expressions of Nernst and changes in the Gibbs energy [3, 11], according to the formula (5):

$$
E_i = \frac{\Delta G_{1,T}}{2F} = \frac{\Delta G_{1,T}^0}{2F} + \frac{R_T}{2F} \ln \left( \frac{p_{O_2}}{p_{O_2}^0} \right) \cdot \left( \alpha_1 \right)^{-1},
$$

(5)

where $F$ – Faraday constant, C/mol.

The change in the Gibbs energy of the decomposition of boric anhydride is determined for the temperature at which boration is carried out, taking into account the change in this energy under standard conditions and the chemical potentials of the reacting substances, as well as the resulting phase transitions and sublimation. This change in the Gibbs energy is determined taking into account the Van't Hoff equation [4, 7, 10] by formula (6):
\[ \Delta G_{2,T} = \Delta G_{2,T}^0 + R_T \ln \left( \left( \frac{p_{O_2}}{2} \right)^{1.5} \cdot \left( \alpha_2 \right)^{-1} \right), \]  

(6)

where \( \Delta G_{2,T}^0 \) – the change in the Gibbs energy of the decomposition reaction of boric anhydride under standard conditions, J/mol; \( \alpha_2 \) – the activity of boric anhydride at operating temperature.

The change in the Gibbs energy under standard conditions is calculated taking into account the enthalpy and entropy of the decomposition reaction of boric anhydride \([3, 4, 5, 6, 7, 10]\) according to formula (7):

\[ \Delta G_{2,T}^0 = \Delta H_{2,T}^0 - T \Delta S_{2,T}^0, \]  

(7)

where \( \Delta H_{2,T}^0 \) – the enthalpy of decomposition of boric anhydride at standard temperature, J/mol; \( \Delta S_{2,T}^0 \) – the change in entropy, decomposition reaction of boric anhydride, at standard temperature, J/ºC-mol.

The enthalpy of the decomposition reaction of boric anhydride at the borating temperature is determined by formula (8):

\[ \Delta H_{2,T}^0 = \Delta H_{2,T}^0 + \int_{p_{T2}}^{T} C_p^b dT \pm \Delta H_{p22}, \]  

(8)

where \( C_p^b \) – the specific heat capacity for the decomposition reaction of boric anhydride, J/ºC-mol; \( \Delta H_{p22} \) – the enthalpy of phase transitions of boric anhydride (at the corresponding temperatures \( T_{p22} \), J/mol.

The entropy of the decomposition reaction of boric anhydride at operating temperature is determined by the formula (9):

\[ \Delta S_{2,T}^0 = \Delta S_{2,T}^0 + \int_{p_{T2}}^{T} \frac{C_p^b}{T} dT \pm \frac{\Delta H_{p22}}{T_{p22}}. \]  

(9)

The electromotive force of polarization of boric anhydride in this case is calculated, taking into account the expression for determining the change in the Gibbs energy and the Nernst formula \([3, 4, 5, 6, 7, 10]\) by the formula (10):

\[ E_2 = \frac{\Delta G_{2,T}}{6F} = \frac{\Delta G_{2,T}^0}{6F} + \frac{R_T}{2F} \ln \left( \left( \frac{p_{O_2}}{2} \right)^{0.5} \cdot \left( \alpha_2 \right)^{-0.33} \right). \]  

(10)

The sequence of the release of boron and sodium at the cathode is determined by a quantitative comparison of the electromotive forces of polarization of boric anhydride and sodium oxide (11):

\[ E_1 - E_2 = \frac{3\Delta G_{1,T}^0 - \Delta G_{2,T}^0}{6F} + \frac{R_T}{2F} \ln \left( \left( \frac{p_{O_2}}{2} \right)^{0.5} \cdot \left( \alpha_2 \right)^{-0.33} \right). \]  

(11)

Based on the anionic and cationic composition of the molten working and heating medium, the energy of chemical bonds between them and the structure model, a mathematical model is formulated. It is based on the determination of the Gibbs free energy using the theory of regular solutions, which takes into account the interaction of boron and sodium cations with the oxygen anion, as well as their energy and entropy change.

The average bond energy of sodium cations with oxygen ions, in accordance with the mixing rule, is described by expression (12):

\[ u_1 = \phi_1 u_{11} + \phi_2 u_{12}, \]  

(12)

where \( u_{11} \) – the bond breaking energy of the sodium cation, surrounded by sodium cations, with oxygen anion, J; \( u_{12} \) - the bond breaking energy of the sodium cation surrounded by boron cations.
with the oxygen, anion, \( J_1 \) and \( J_2 \) – the molar fractions of sodium and boron ions, respectively.

The average bond energy of a boron cation with an oxygen ion is determined similarly by formula (13):

\[
u_2 = \phi_1 u_{21} + \phi_2 u_{22},
\]

where \( u_{21} \) – the bond breaking energy of a boron cation surrounded by sodium cations, with an oxygen anion, \( J_1 \); \( u_{22} \) – the bond breaking energy of a boron cation surrounded by boron cations with an oxygen anion, \( J_2 \).

Chemical bonds between all ions of one mole of a molten working and heating medium have an energy that is determined by expression (14):

\[
U^{cb} = N_A (\phi_1 u_1 + \phi_2 u_2),
\]

where \( N_A \) – Avogadro’s number, mol\(^{-1}\).

This energy depends on the mutual arrangement of cations and anions and is the sum of the energies of all boron and sodium cations, as well as oxygen anions [3, 4, 5, 6, 7, 10].

As a result, we get the expression (15):

\[
U^{cb} = \phi_1 U_1^{cb} + \phi_2 U_2^{cb} + \phi_1 \phi_2 Q_d,
\]

where \( U_1^{cb} \) and \( U_2^{cb} \) - the energy of sodium oxide and boric anhydride, respectively, \( J_1 \); \( Q_d \) - the displacement energy, \( J_1 \).

Taking into account the Boltzmann equation and Stirling’s formula [9], the entropy of the system is determined by the formula (16):

\[
S^s = \phi_1 S_1^0 + \phi_2 S_2^0 - R_d (\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2).
\]

The Gibbs free energy of one mole of the molten working and heating medium is determined by the formula (17):

\[
G^d_i = \phi G_{1/2m}^d + \phi G_{1/2m}^d + R_T (\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2) + \phi_1 \phi_2 Q_d,
\]

where \( G_{1/2m}^d \) – the free energy, calculated for 0.5 mol of sodium oxide, \( J_1 \); \( G_{1/2m}^d \) – the free energy, calculated for 0.5 mol of boric anhydride, \( J_1 \).

The free energy of the molten working and heating medium consisting of an arbitrary number of moles of sodium oxide and boric anhydride is determined by the formula (18):

\[
G_n^d = 2(n_1 G_{1/2m}^d + n_2 G_{2/2m}^d + R_T (n_1 \ln \phi_1 + n_2 \ln \phi_2) + n_1 n_2 (\phi_1 + \phi_2)^{-1} Q_d),
\]

where \( n_1 \) and \( n_2 \) – the number of moles of sodium oxide and boric anhydride in the composition of the working and heating medium, respectively.

The chemical potentials of sodium oxide and boric anhydride are actually the free energies of one mole of each substance in the working and heating medium. To determine them, it is necessary to take the partial derivatives of expression (18), first by \( n_1 \) (19), and then by \( n_2 \) (20):

\[
\frac{\partial G_n^d}{\partial n_1} = \phi_1 \ln \phi_1 + 2 \phi_1 + 2(\phi_2)^{-1} Q_d,
\]

\[
\frac{\partial G_n^d}{\partial n_2} = \phi_2 \ln \phi_2 + 2 \phi_2 + 2(\phi_1)^{-1} Q_d.
\]

where \( \phi_1 \) and \( \phi_2 \) - the standard chemical potentials of sodium oxide and boric anhydride, respectively, J/mol; \( \phi_1 \) and \( \phi_2 \) - the chemical potentials of sodium oxide and boric anhydride, respectively, J/mol.

This allows us to obtain expressions for determining the activity of sodium oxide (21) and boric...
anhydride (22) at their arbitrary concentration in the melt:

\[ \alpha_1 = \left( \phi_1 \right)^2 \exp \left( 2 \left( \phi_2 \right)^2 Q_d \cdot \left( R_u T \right)^{-1} \right), \tag{21} \]

\[ \alpha_2 = \left( \phi_3 \right)^2 \exp \left( 2 \left( \phi_4 \right)^2 Q_d \cdot \left( R_u T \right)^{-1} \right). \tag{22} \]

The value of the energy of mixing of ions is carried out taking into account the thermal effect of the formation of sodium tetraborate from oxides. The enthalpy of this reaction is determined for the borating temperature [3, 4, 5, 6, 7, 10] taking into account the enthalpy of phase transitions from the crystalline to the molten state of oxides and sodium tetraborate itself during its formation (23):

\[ \Delta H_{\Omega,T} = \Delta H^0_{\Omega,T} + T \int_{T_0}^{T} \Delta C^\text{p} dT \pm \Delta H_{\text{pt}}, \tag{24} \]

where \( \Delta H^0_{\Omega,T} \) – the enthalpy of reaction of sodium tetraborate at borating temperature, J/mol;

\[ \Delta H^0_{\Omega,T} = \Delta H^0_{\Omega,T} + T \Delta C^\text{p} dT \pm \Delta H_{\text{pt}}, \tag{25} \]

where \( \Delta C^\text{p} \) – the total change in heat capacities, J/mol.

The enthalpy of this reaction (taking into account \( \Delta H^0_{\Omega,T} \)) in accordance with the Gibbs free energy formula (1) is determined by the expression (26):

\[ Q_d = 0.75 \cdot \Delta H^s. \tag{26} \]

As a result, we obtain a formula for determining the difference in the electromotive force of polarization of the corresponding electrolytic cells of boron and sodium (27):

\[ E_1 - E_2 = \frac{3 \Delta C^0_{1/2} - \Delta C^0_{2/3}}{6F} + \frac{RT}{F} \ln \left( \frac{\left( \phi_3 \right)^{0.33}}{\left( \phi_4 \right)^{0.33}} \right) + \left( 0.33 \left( \phi_3 \right)^2 - \left( \phi_4 \right)^2 \right) \frac{Q_d}{F}. \tag{27} \]

3. Results

The calculation results according to the formulas (1) - (27) are summarized in the following table.

| Change in Gibbs energy of the decomposition reaction of: | Mole fraction of sodium cations | Mole fraction of boron cations | Mixing energy, kJ | PolariZation EMF, V | Boron cation concentration, mol/m³ |
|---------------------------------------------------|---------------------------------|-------------------------------|-----------------|----------------|-------------------------------|
| sodium oxide, kJ/mol                               | 0.26                            | 0.74                          | -293            | 1.316           | 14.8·10³                      |
| boric anhydride, kJ/mol                            |                                 |                               |                 |                |                               |
4. Conclusion
As a result of the calculation, it turns out that sodium oxide is more stable than boric anhydride \((E_1 - E_2 > 0)\). In the case of electrolysis of such melts, when a higher decomposition voltage of boric anhydride and a lower decomposition voltage of sodium oxide are applied to the cell, active boron atoms are reduced from cations on the cathode surface. Consequently, the calculated substantiation of the application of the proposed composition for strengthening and restoring parts confirmed the possibility of its use.

References
[1] Akhmetshin T F 2014 Prediction of the durability of the blades of lancet paws of cultivators Bulletin of the Orenburg State Agrarian University 5 (49) 74
[2] Builov V N 2019 Calculation assessment of the use of electrolyte melts in strengthening the restored working bodies of tillage and sowing aggregates Agricultural scientific journal 5 77
[3] Bartenev I M, Pozdnyakov E V 2013 The deteriorating ability of soils and its effect on the durability of the working bodies of tillage machines Forestry magazine 3 (11) 114
[4] Lebedev K A, Lebedev A L 2015 Increasing the resource of cultivator paws Scientific Review 3 50
[5] Lyalyakin V P, Soloviev S A, A V Aulov 2014 The state and prospects of hardening and restoration of parts of tillage machines by welding and surfacing methods Welding production 7 32
[6] Buylov V N, Lyulyakov I V, Eremenko V S, Pronin S A 2017 To the question of working conditions and wear of lancet paws of cultivators Actual problems of scientific and technological progress in the agro-industrial complex: Sat. scientific articles under the general ed A T Lebedev (Stavropol: AGRUS) pp 3–5.
[7] Novikov V S, Petrovsky D I 2017 Increasing the durability of lancet paws of cultivators Bulletin of FGOU VPO MGAU im. V P Goryachkina. 4 55
[8] Rusinov A V, Slyusarenko V V 2015 Change of physical and mechanical properties of reclamation soils as a result of mechanical action Innovations in environmental management and protection in emergency situations: Materials of the II international scientific and practical conference ed A V Rusinov (Saratov: KUBiK) pp 30–33
[9] Tenenbaum M M, Shamsheev S N 1986 Wear resistance and durability of agricultural machines (Nukus: Karakalpakstan)
[10] Tkachev V N, Kazintsev N V, Zagrebin A V 1991 Increasing the durability of tillage working bodies Tractors and agricultural machines 12 46
[11] Kragelsky I V, Dobychin M N, Kombalov V S 1977 Fundamentals of calculation for friction and wear (Moscow: Mechanical Engineering)