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Thermodynamic Simulation of the Flux Refining of Primary Aluminum in a Ladle

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Abstract—The processing of primary aluminum with boric acid in a ladle is subjected to thermodynamic analysis. The HSC Chemistry 9.0 (Outotec Technologies) software was used for calculations. The temperature range investigated in the calculations (650–950°C) corresponds to the production conditions of the Kazakhstan Electrolysis Plant. The pressure range is determined using the technological conditions of flux treatment of aluminum in a crane ladle with a working height of 2 m and ranged from 101.33 to 148.99 kPa. The presence of a solid phase and low process kinetics are characterized by the lower limit of the temperature range. The upper limit of temperatures demonstrates the conditions closest to the actual working conditions during electrolysis. The pressure at the metal melt surface is represented by the lower limit in the pressure range, and the pressure at the depth of flux immersion equivalent to 2 m is represented by the upper limit. The depth of the suspension immersion in the calculations is varied in the range 0.5–2 m. The thermodynamic analysis in the investigated range of temperatures and pressures unequivocally indicates that vanadium borides are more stable compared to aluminum borides; therefore, they will predominantly form in this temperature range. The stability order also suggests that vanadium can be easily removed from aluminum melts by adding boron.

Keywords: aluminum, thermodynamic simulation, flux, boric acid, refining

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INTRODUCTION

The coke produced by TOO UPNK-PV (Pavlodar) is partly involved in the production of anodes for the electrolytic baths at the Kazakhstan Electrolysis Plant (KEZ). The locally produced coke contains a high content of vanadium and other impurities, which in turn limits its use at the plant.

A literature review has shown that there are methods of refining primary aluminum from vanadium impurities using boron compounds, which have not been widely used industrially [1–15].

The chemical reactions in the Al–V–B system are known to have a complex character [13–15]. The VB_2 compounds are thermodynamically stable at the operating temperatures of electrolysis and aluminum casting (950–650°C). The kinetics of chemical reactions with the formation of the VB_2 compounds during refining with Al–B master alloys is characterized by a low rate due to the formation of an insoluble ring of reaction products consisting of vanadium diboride (VB_2).

THERMODYNAMIC SIMULATION

In the study, the processing of primary aluminum with boric acid using the technique from [16] is subjected to thermodynamic analysis. The calculations were performed using the HSC Chemistry 9.0 (Outotec Technologies) software.

During the refining of the raw aluminum melt with boric acid at temperatures ranging from 650 to 950°C and a pressure of about 101.33 kPa, boric acid (H_3BO_3) undergoes transformation into boron oxide (B_2O_3), which then reacts with the aluminum melt and further with vanadium compounds according to the following equations:

$$B_2O_3 + 3Al \rightarrow AlB_2 + Al_2O_3, \quad (1)$$

$$AlB_2 + Al_3V = VB_2 + 4Al, \quad (2)$$

$$AlB_2 + V = VB_2 + Al. \quad (3)$$

In the calculations, the considered temperature range corresponded to the production conditions of AO KEZ within the range 650–950°C. The range of

Table 1. Calculated values of C_p, ΔG, ΔH, ΔS for the AlB_2 and VB_2 compounds

Compound	Parameter	Range of calculated temperatures, °C (at pressure of 102.39 kPa)						
		650°C	700°C	750°C	800°C	850°C	900°C	950°C
AlB_2	C_p	75.764	77.363	78.938	80.494	82.033	83.560	85.075
	ΔH	23.587	27.416	31.323	35.309	39.372	43.512	47.728
	S	103.132	107.171	111.086	114.889	118.590	122.196	125.715
	ΔG	−71.619	−76.877	−82.334	−87.984	−93.821	−99.841	−106.039
VB_2	C_p	79.019	80.232	81.361	82.409	83.381	84.277	85.524
	ΔH	−161.700	−157.719	−153.678	−149.584	−145.439	−141.247	−137.004
	S	102.968	107.168	111.216	115.123	118.898	122.549	126.090
	ΔG	−256.755	−262.009	−267.469	−273.128	−278.979	−285.016	−291.232

pressures was determined based on the technological conditions of flux treatment of aluminum in a distribution ladle with a working height of 2 m within the range of 101.33–148.99 kPa. The presence of a solid phase and low process kinetics is characterized by the lower limit of the specified range. The upper limit demonstrates conditions closest to real working conditions during electrolysis. The pressure at the metal surface represents the lower limit in the range, while the pressure at the depth of immersion of the flux equivalent to 2 m represents the upper limit. The depth of immersion of the charge varies according to the ladle height and ranged from 0.5 to 2 m. The temperature range was selected in accordance with the working conditions in the workshop: from 650 to 950°C, corresponding to the highest aluminum melt density (2380 kg/m^3) in the temperature range under study.

RESULTS AND DISCUSSION

The calculation of thermodynamic parameters was carried out for the AlB_2 and VB_2 compounds. Table 1 and Fig. 1 present the calculated values of C_p, ΔG, ΔH, and ΔS.

At temperatures ranging from 650 to 950°C and atmospheric pressure, the change in the Gibbs energy for the VB_2 compound is −256.755 and −291.232 kJ/mol, and for AlB_2 it is −71.619 and −106.039 kJ/mol, respectively. The change in enthalpy is negative for the reactions of vanadium diboride, indicating an exothermic nature of the formation of this compound, while the formation of aluminum diboride is endothermic due to the positive enthalpy.

In addition, the thermodynamic parameters for the chemical reaction $AlB_2 + V = VB_2 + Al$ were calcu-

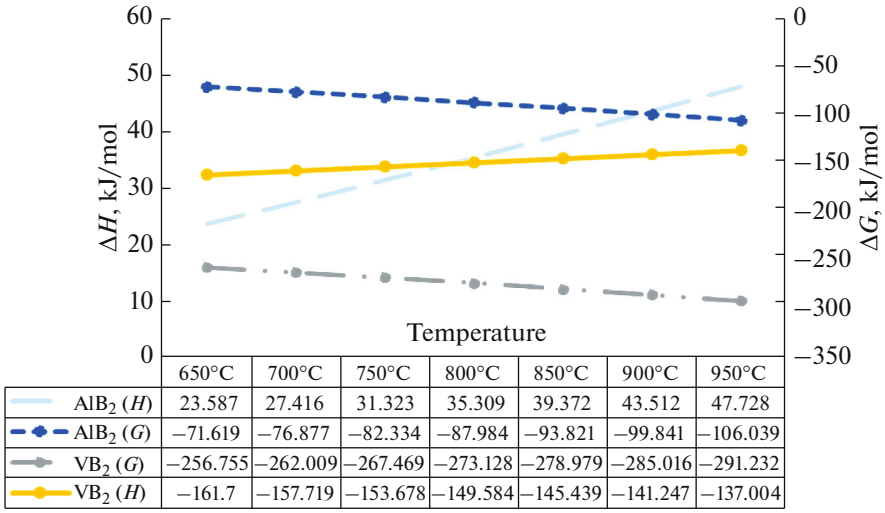
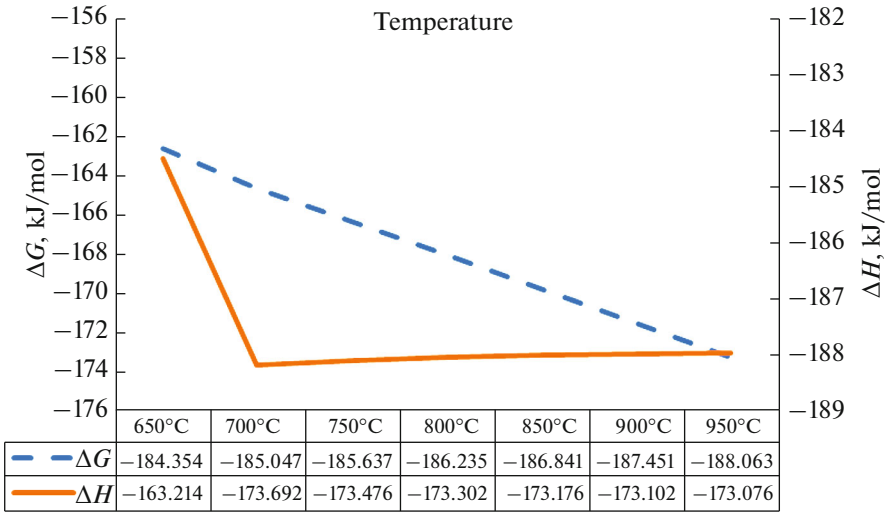
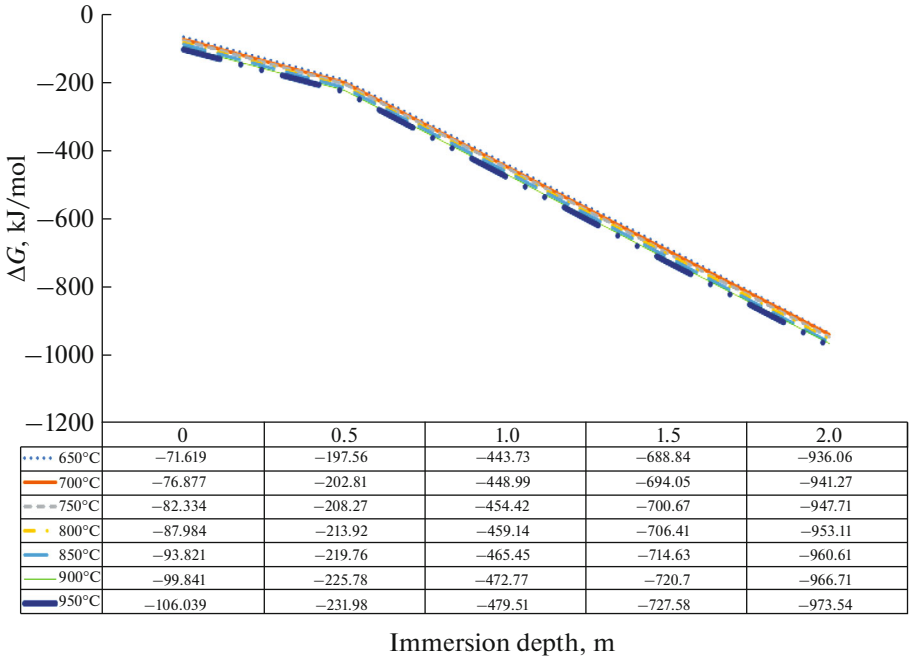


Fig. 1. Gibbs energy and enthalpy for VB_2 and AlB_2 as a function of temperature.



	650°C	700°C	750°C	800°C	850°C	900°C	950°C
ΔG	−184.354	−185.047	−185.637	−186.235	−186.841	−187.451	−188.063
ΔH	−163.214	−173.692	−173.476	−173.302	−173.176	−173.102	−173.076

Fig. 2. Gibbs energy and enthalpy for the chemical reaction $AlB_2 + V = VB_2 + Al$ as a function of temperature.



	0	0.5	1.0	1.5	2.0
650°C	−71.619	−197.56	−443.73	−688.84	−936.06
700°C	−76.877	−202.81	−448.99	−694.05	−941.27
750°C	−82.334	−208.27	−454.42	−700.67	−947.71
800°C	−87.984	−213.92	−459.14	−706.41	−953.11
850°C	−93.821	−219.76	−465.45	−714.63	−960.61
900°C	−99.841	−225.78	−472.77	−720.7	−966.71
950°C	−106.039	−231.98	−479.51	−727.58	−973.54

Fig. 3. Gibbs energy for VB_2 and AlB_2 as a function of temperature and immersion depth of boron based flux into aluminum depth.

lated. Table 2 and Fig. 2 present the calculated values of ΔG, ΔH, ΔS, and log$k$.

The analysis of thermodynamic parameters confirms that at atmospheric pressure and temperatures from 650 to 950°C, the reaction $AlB_2 + V = VB_2 + Al$ proceeds with the formation of vanadium diboride (VB_2), and the change in Gibbs energy is −184.354 and −188.676 kJ/mol, respectively. The increase in Gibbs energy with increasing temperature indicates an increase in the stability of the chemical reactions. The overall change in enthalpy is negative, indicating an exothermic nature of the formation of these compounds. It can be concluded that the chemical reaction proceeds with a thermodynamically favorable character.

Furthermore, a thermodynamic analysis was conducted for the conditions of flux immersion into the melt at depths of 0.5, 1, 1.5, and 2 m.

Table 3 and Fig. 3 present the calculated values of Gibbs energy for VB_2 and AlB_2 compounds.

At a temperature of 650°C and pressures of 102.39 kPa (at the surface of the melt) and 148.99 kPa (at a depth of 2 m for the flux addition), the change in the Gibbs energy for VB_2 formation is −256.755 and

Table 2. Calculated values of ΔG, ΔH, ΔS, log k for the chemical reaction $AlB_2 + V = VB_2 + Al$

Chemical reaction	Parameter	Range of calculated temperatures, °C (at pressure of 102.39 kPa)						
		650°C	700°C	750°C	800°C	850°C	900°C	950°C
$AlB_2 + V = VB_2 + Al$	ΔH	−163.214	−173.692	−173.476	−173.302	−173.176	−173.102	−173.076
	S	22.900	11.668	11.885	12.051	12.166	12.232	12.253
	ΔG	−184.354	−185.047	−185.637	−186.235	−186.841	−187.451	−188.063
	log$k$	10.432	9.933	9.478	9.066	8.690	8.347	8.032

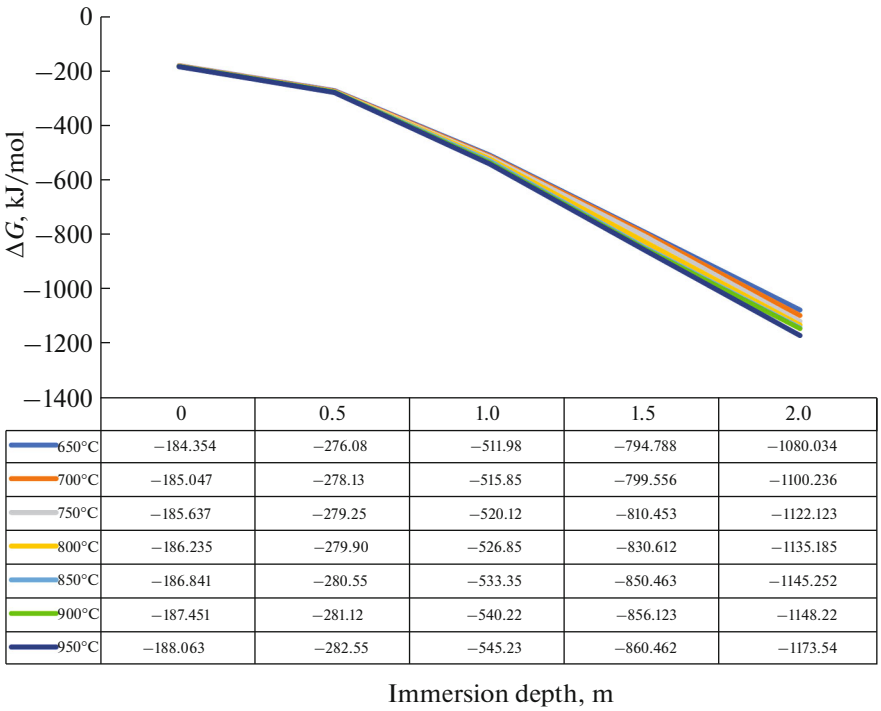
Table 3. ΔG for AlB_2 and VB_2 compounds at depths of 0.5, 1, 1.5, and 2 m

Compound	Flux immersion depth into melt, m	Range of calculated temperatures, °C						
		650°C	700°C	750°C	800°C	850°C	900°C	950°C
AlB_2	0.5	−197.56	−202.81	−208.27	−213.92	−219.76	−225.78	−231.98
	1.0	−443.73	−448.99	−454.42	−459.14	−465.45	−472.77	−479.51
	1.5	−688.84	−694.05	−700.67	−706.41	−714.63	−720.70	−727.58
	2.0	−936.06	−941.27	−947.71	−953.11	−960.61	−966.71	−973.54
VB_2	0.5	−307.17	−312.42	−317.88	−323.54	−329.39	−335.43	−341.64
	1.0	−689.91	−694.82	−700.28	−706.13	−713.28	−719.41	−726.74
	1.5	−1070.94	−1076.01	−1083.34	−1091.45	−1100.63	−1107.26	−1118.38
	2.0	−1455.38	−1461.57	−1468.48	−1475.58	−1485.12	−1491.89	−1511.17

−1455.3 kJ/mol, respectively. For AlB_2 compound under these conditions, the change in Gibbs energy is −71.619 and −936.06 kJ/mol for the initial temperature and −291.232 and −1511.17 kJ/mol for a temperature of 950°C and VB_2, repsectively, and −106.039 and −973.54 kJ/mol for AlB_2.

Further thermodynamic calculations were performed on the change in the isobaric–isothermal potential of the system for the chemical reaction $AlB_2 + V = VB_2 + Al$.

Table 4 and Fig. 4 present the calculated values of Gibbs energy for the chemical reaction $AlB_2 + V = VB_2 + Al$.



	0	0.5	1.0	1.5	2.0
650°C	−184.354	−276.08	−511.98	−794.788	−1080.034
700°C	−185.047	−278.13	−515.85	−799.556	−1100.236
750°C	−185.637	−279.25	−520.12	−810.453	−1122.123
800°C	−186.235	−279.90	−526.85	−830.612	−1135.185
850°C	−186.841	−280.55	−533.35	−850.463	−1145.252
900°C	−187.451	−281.12	−540.22	−856.123	−1148.22
950°C	−188.063	−282.55	−545.23	−860.462	−1173.54

Fig. 4. Gibbs energy for the chemical reaction $AlB_2 + V = VB_2 + Al$ as a function of temperature and immersion depth of boron based flux into aluminum depth.

Table 4. ΔG for the chemical reaction $AlB_2 + V = VB_2 + Al$ at depths of 0.5, 1, 1.5, and 2 m

Compound	Flux immersion depth into melt, m	Range of calculated temperatures, °C						
		650°C	700°C	750°C	800°C	850°C	900°C	950°C
$AlB_2 + V = VB_2 + Al$	0	−184.354	−185.047	−185.637	−186.235	−186.841	−187.451	−188.063
	0.5	−276.08	−278.13	−279.25	−279.90	−280.55	−281.12	−282.55
	1.0	−511.98	−515.85	−520.12	−526.85	−533.35	−540.22	−545.23
	1.5	−794.788	−799.556	−810.453	−830.612	−850.463	−856.123	−860.462
	2.0	−1080.034	−1100.236	−1122.123	−1135.185	−1145.252	−1148.22	−1173.54

At a temperature of 650°C (Figs. 4 and 5), for pressures of 102.39 kPa (at the surface of the melt) and 148.99 kPa (at a depth of 2 m for the flux addition), the change in Gibbs energy for the chemical reaction $AlB_2 + V = VB_2 + Al$ is −184.354 and −1080.034 kJ/mol, respectively. At a temperature of 950°C, these values are −188.063 and −1173.54 kJ/mol.

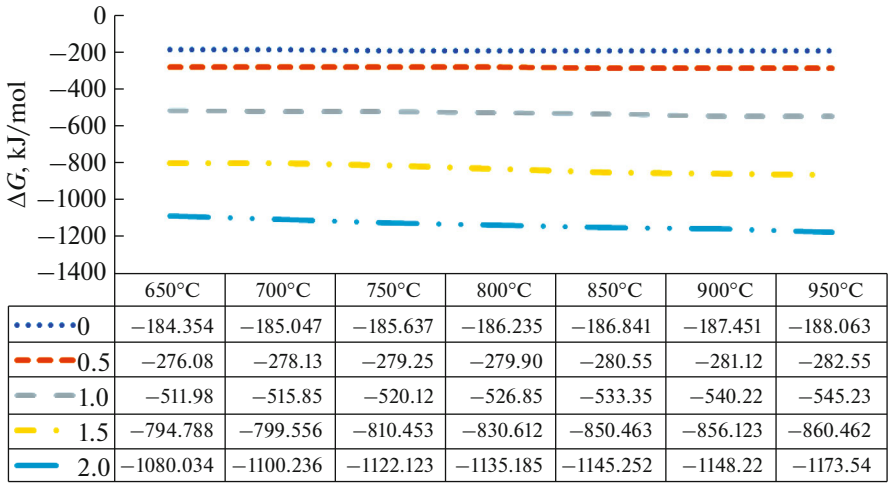
This important observation shows that as pressure increases at constant temperature, the difference in changes in the isobaric–isothermal potential decreases, especially at higher temperatures. On the other hand, as temperature decreases at constant pressure, the difference in the changes in Gibbs energy also decreases, and this trend is more noticeable with increasing pressure in the system.

At a temperature of 650°C (Figs. 4, 5), for the reaction $AlB_2 + V = VB_2 + Al$, the difference in the changes in Gibbs energy when increasing pressure in the system from 102.39 to 114.04 kPa is −91.726 kJ/mol, from 114.04 to 125.69 kPa is −235.9 kJ/mol, from 125.69 to 137.29 kPa is −282.808 kJ/mol, and from 137.29 to 148.99 kPa is −285.246 kJ/mol. At a temperature of 950°C, these changes in the Gibbs energy are −94.487, −262.68, −315.232, and −313.078 kJ/mol, respectively.

This observation highlights that the chemical reactions of interaction of primary aluminum and impurities, including vanadium with boron to form intermetallic compounds, can proceed in a specific direction within the temperature and pressure range under study (Fig. 6).

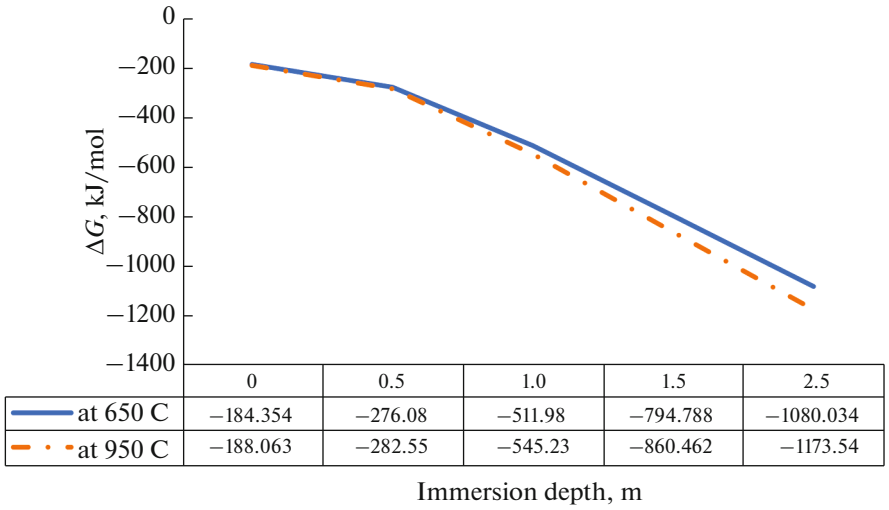
CONCLUSIONS

At temperatures of 650–950°C and atmospheric pressure, the change in the Gibbs energy for the VB_2 compounds is −256.755 and −291.232 kJ/mol, and for AlB_2 is −71.619 and −106.039 kJ/mol. Thermodynamic analysis with the HSC Chemistry 9.0 software for the Al–V, Al–B, V–B systems in the temperature and pressure range under study showed that the Gibbs



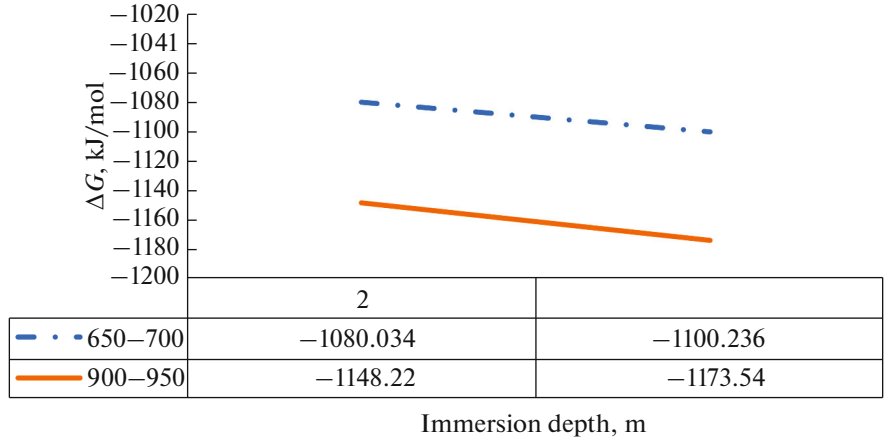
	650°C	700°C	750°C	800°C	850°C	900°C	950°C
0	−184.354	−185.047	−185.637	−186.235	−186.841	−187.451	−188.063
0.5	−276.08	−278.13	−279.25	−279.90	−280.55	−281.12	−282.55
1.0	−511.98	−515.85	−520.12	−526.85	−533.35	−540.22	−545.23
1.5	−794.788	−799.556	−810.453	−830.612	−850.463	−856.123	−860.462
2.0	−1080.034	−1100.236	−1122.123	−1135.185	−1145.252	−1148.22	−1173.54

Fig. 5. ΔG for the chemical reaction $AlB_2 + V = VB_2 + Al$ as a function of temperature at fixed increase in immersion depth of boron based flux into aluminum melt.



	0	0.5	1.0	1.5	2.5
at 650 C	−184.354	−276.08	−511.98	−794.788	−1080.034
at 950 C	−188.063	−282.55	−545.23	−860.462	−1173.54

Fig. 6. ΔG for the chemical reaction $AlB_2 + V = VB_2 + Al$ as a function of immersion depth of boron based flux into aluminum melt during variation of temperature.



	2	
650–700	−1080.034	−1100.236
900–950	−1148.22	−1173.54

Fig. 7. Isobaric–isothermal potential of reaction as a function of flux immersion depth.

energy (ΔG) over the entire operating temperature range for the electrolysis and casting of primary aluminum for VB_2 is significantly lower than for AlB_2; therefore, it will predominantly form in this temperature range. The stability order also suggests that vanadium can be easily removed from aluminum melts by adding boron. In the temperature range 650–950°C and the pressure range 102.34–149.88 kPa, the vanadium boride phases are more stable compared to aluminum borides; therefore, they will predominantly form in this temperature range. The stability order also suggests that vanadium can be easily removed from aluminum melts by adding boron.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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