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THERMODYNAMIC ANALYSIS OF THE POSSIBLE EXISTENCE OF THE TERNARY $Ba_3CoAl_4O_{10}$ COMPOUND IN THE $BaO-CoO-Al_2O_3$ SYSTEM

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The work was aimed at the thermodynamic estimation of the possible existence of ternary compound $Ba_3CoAl_4O_{10}$ in the $BaO-CoO-Al_2O_3$ system. To this end, the composition of the expected ternary compound was calculated considering that this compound should be located in the $CoAl_2O_4-Ba_3Al_2O_6$ conode. With reference to this, the temperature and the eutectic composition in the binary section of $CoAl_2O_4-Ba_3Al_2O_6$ were estimated. The standard enthalpy of the formation of the above three-component compound, the standard entropy and the coefficients of the temperature dependence of the heat capacity were calculated. Using the method developed by Babushkin, the temperature dependence of the Gibbs energy for the formation of $Ba_3CoAl_4O_{10}$ compound was determined for the range of 800 to 2000 K. The probability of the $Ba_3CoAl_4O_{10}$ formation was evaluated both for its preparation both from pure aluminum, cobalt and barium oxides and from barium carbonate, aluminum and cobalt oxides. In addition, the probability of the $Ba_3CoAl_4O_{10}$ formation from binary compounds $CoAl_2O_4$ and $Ba_3Al_2O_6$ was estimated. The possible formation of the ternary compound from $Ba_3Al_2O_6$, $BaAl_2O_4$ and CoO was also considered, because the $Ba_3CoAl_4O_{10}$ compound is located in this triangle. The graphs of the change of Gibbs energy with temperature (800–2000 K) were plotted for all reactions. The obtained results showed that the formation of the ternary compound from barium, aluminum and cobalt oxides is more feasible from the standpoint of thermodynamics than from the binary compounds.

Keywords: thermodynamic analysis, $BaO-CoO-Al_2O_3$ system, ternary compound $Ba_3CoAl_4O_{10}$, Gibbs energy, eutectic.

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Introduction

It is known that thermodynamic analysis of the subsolidus structure of multicomponent oxide systems is an efficient theoretical method used for the determination of the optimal domains that provide the production of cementing material with specified properties. To produce refractory cementing materials with a high corrosion and ionizing radiation resistances, the $BaO-CoO-Al_2O_3$ system attracts particular interest, because it includes barium aluminates and cobalt spinel that would impart an increased refractoriness and ionizing radiation resistance to the developed cements. Therefore, the study of the interaction reactions of the basic raw components of the above ternary oxide system at different temperatures are highly topical.

Earlier, the triangulation of the ternary oxide system $BaO-CoO-Al_2O_3$ was performed using thermodynamic method of analysis [1]. We analyzed the solid-phase reactions in the $BaO-CoO-Al_2O_3$ system; the geometric and topological characteristics were given for the system and its phases. The theoretical studies showed that an optimal domain for the production of cementing materials with an increased fire and ionizing radiation resistances is circumscribed by the points of $CoO-BaAl_2O_4-CoAl_2O_4$ compositions, because particularly this triangle has the largest area and corresponds to the phases with the highest probability of the existence. However, ref. [1] did not take into account the availability of any other compounds, except for initial oxides and known binary barium and cobalt aluminates.

Meanwhile, literature data [2–4] show that the existence of a ternary component $Ca_3CoAl_4O_{10}$ is feasible in the calcium-containing system

$CaO-CoO-Al_2O_3$, therefore it was assumed that the ternary compound $Ba_3CoAl_4O_{10}$ can exist in the ternary system $BaO-CoO-Al_2O_3$. Hence, the purpose of this research was to ascertain thermodynamically the possibility of the existence of a ternary compound $Ba_3CoAl_4O_{10}$ in the $BaO-CoO-Al_2O_3$ system.

Results and discussion

We calculated the composition of a presumptive ternary component positioned in the $CoAl_2O_4-Ba_3Al_2O_6$ conode. In this connection, we determined the temperature and eutectic composition in the binary section $CoAl_2O_4-Ba_3Al_2O_6$. The temperatures and compositions of eutectics in binary sections were calculated using the Epstein-Howland formulas using BINevt vl.3 software [5].

The performed calculations showed that the eutectic composition in the $CoAl_2O_4-Ba_3Al_2O_6$ section is similar to that of a ternary component ($Ba_3Al_2O_6$ 85 wt.% and $CoAl_2O_4$ 15 wt.%). Hence, the melting temperature of the ternary compound $Ba_3CoAl_4O_{10}$ is close to that of the eutectic in the binary section $CoAl_2O_4-Ba_3Al_2O_6$; it is equal to 1946 K.

Due to the lack of literature data on the basic thermodynamic characteristics of the ternary compound $Ba_3CoAl_4O_{10}$, we calculated the standard enthalpy of its formation, the standard entropy and the heat capacity-temperature coefficients.

The methods developed by Morachevsy and Sladkov [6] were used to calculate the standard enthalpy of formation; it takes into consideration the average gram-atomic enthalpy of the formation of compounds of this ternary system. An average value of the standard enthalpy of the formation of the ternary $Ba_3CoAl_4O_{10}$ compounds from simple oxides was stated to be $\Delta H^0_{298}=-5358.4735$ kJ/mol.

The standard entropy of the $Ba_3CoAl_4O_{10}$ compound was calculated using the methods developed by Yatsimirsky et al. [6]. The standard entropy of the ternary compound under consideration was $\Delta S^0_{298}=171.9$ J/mol·K.

The coefficients in the equation «heat capacity vs. temperature» were calculated using the method proposed by Landia [7] (no polymorphic transformations were considered for the complex oxygen compounds consisting of solid oxides). Since the melting temperature of the ternary compound was not known, we approximately accepted the eutectic temperature in the $CoAl_2O_4-Ba_3Al_2O_6$ section equal to 1946 K, its chemical composition is similar to that of the ternary component. The calculations allowed deriving the following equation for the temperature dependence of heat capacity:

$$C_p=256.22+147.55\cdot10^{-3}\cdot T-27.4\cdot10^5\cdot T^{-2}$$

Figure 1 illustrates the obtained dependence «heat capacity vs. temperature» for the $Ba_3CoAl_4O_{10}$ compound.

Further, using the method developed by Babushkin [8], we calculated the relationship of the value of Gibbs energy in the temperature range of 800 to 2000 K for the reaction of formation of the $Ba_3CoAl_4O_{10}$ compound. The $Ba_3CoAl_4O_{10}$ formation probability was calculated both for pure aluminum, cobalt and barium oxides and for barium carbonate and aluminum and cobalt oxides as initial reagents. In addition, we calculated the probability of the formation of $Ba_3CoAl_4O_{10}$ from binary compounds $CoAl_2O_4$ and $Ba_3Al_2O_6$. We also took into consideration the possible formation of the ternary

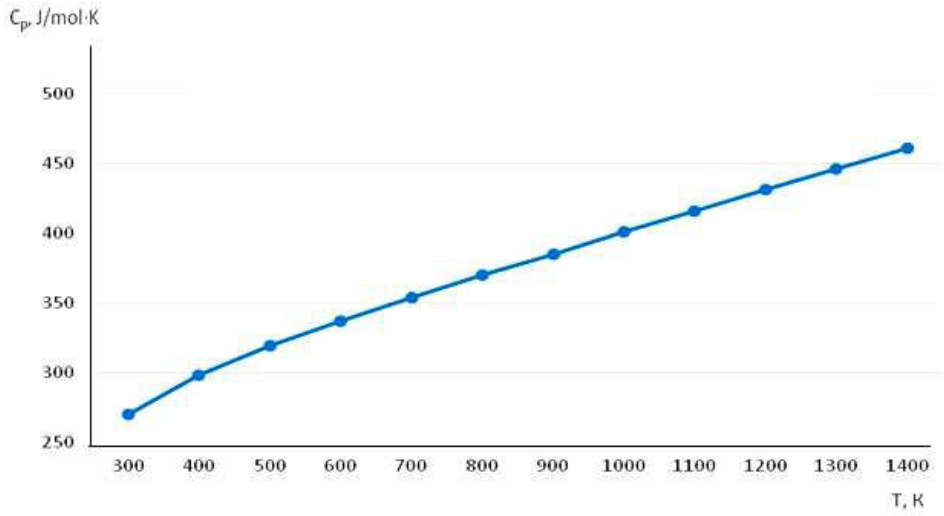
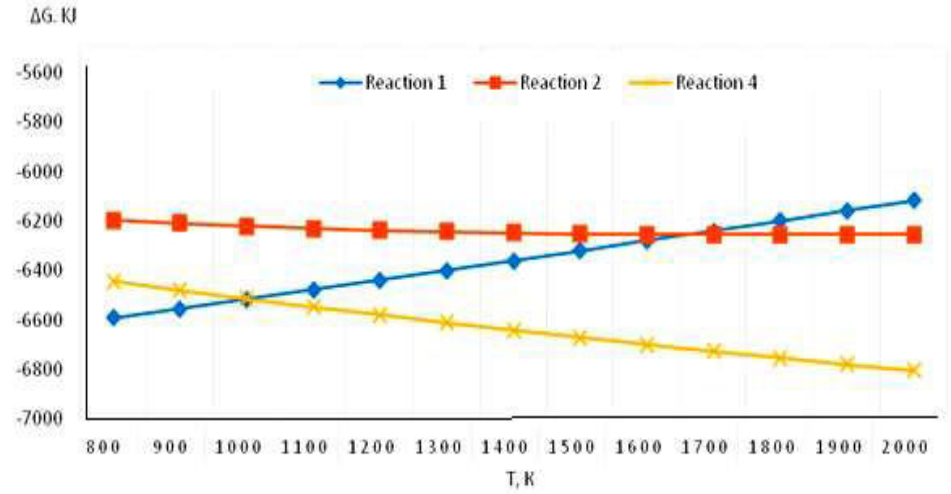


Fig. 1. Calculated heat capacity vs. temperature dependence for the $Ba_3CoAl_4O_{10}$ compound



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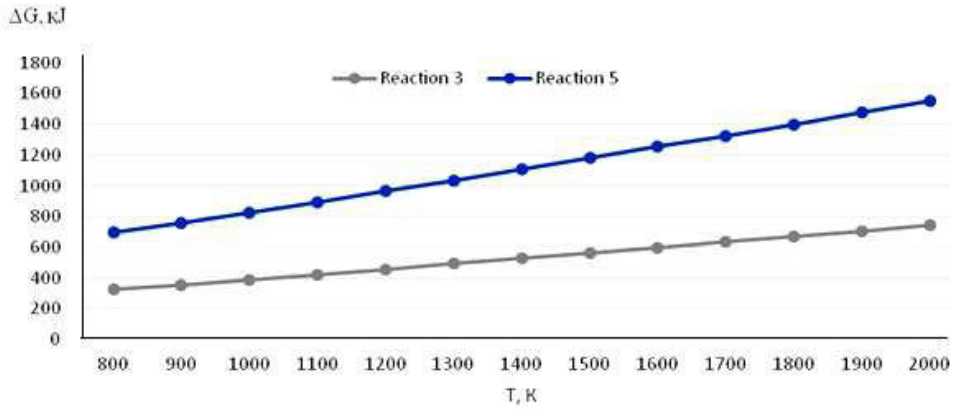

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Fig. 2. Calculated Gibbs energy changes vs. temperature dependences

Calculated changes of Gibbs energy for the reactions of $Ba_3CoAl_4O_{10}$ formation

Temperature, K	ΔG, kJ/mol				
	Reaction number				
	1	2	3	4	5
800	–6589.611	–6196.827	323.575	–6443.696	695.027
900	–6553.415	–6209.436	355.746	–6478.881	759.883
1000	–6516.119	–6220.149	388.818	–6513.068	826.665
1100	–6477.952	–6229.162	422.617	–6546.283	895.043
1200	–6439.098	–6236.635	457.002	–6578.54	964.751
1300	–6399.708	–6242.699	491.856	–6609.865	1035.57
1400	–6359.906	–6247.464	527.083	–6640.258	1107.312
1500	–6319.799	–6251.021	562.599	–6669.734	1179.824
1600	–6279.478	–6253.451	598.334	–6698.300	1252.966
1700	–6239.023	–6254.822	634.223	–6725.963	1326.623
1800	–6198.504	–6255.196	670.213	–6752.729	1400.688
1900	–6157.982	–6254.626	706.254	–6778.602	1475.070
2000	–6117.517	–6253.165	742.301	–6803.589	1549.682

compound from $Ba_3Al_2O_6$, $BaAl_2O_4$ and CoO. The chemical reactions for which the calculations were performed are summarized below:

1) $3BaO+CoO+2Al_2O_3=Ba_3CoAl_4O_{10}$;
2) $3BaCO_3+CoO+2Al_2O_3=Ba_3CoAl_4O_{10}$;
3) $Ba_3Al_2O_6+CoAl_2O_4=Ba_3CoAl_4O_{10}$;
4) $3BaCO_3+CoO+2Al_2O_3=$
$=Ba_3Al_2O_6+CoAl_2O_4+3CO_2$;
5) $Ba_3Al_2O_6+3BaAl_2O_4+2CoO = 2Ba_3CoAl_4O_{10}$.

The calculated changes of Gibbs energy for the given reactions are given in Table. The graphs of Gibbs energy changes at the temperatures of 800 to 2000 K for all reactions are plotted in Fig. 2.

Conclusions

The obtained data showed that the ternary compound $Ba_3CoAl_4O_{10}$ can be formed from both in the reactions between barium, cobalt and aluminum oxides and in the course of the interactions between barium carbonate and aluminum and cobalt oxides in the entire temperature range. However, the formation of $Ba_3CoAl_4O_{10}$ is thermodynamically impossible from $CoAl_2O_4$ and $Ba_3Al_2O_6$ as initial reagents.

Our further study will be directed at the experimental investigation of the synthesis of $Ba_3CoAl_4O_{10}$ compound in the $BaO-CoO-Al_2O_3$ system.

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ТЕРМОДИНАМІЧНИЙ АНАЛІЗ ЙМОВІРНОСТІ ІСНУВАННЯ ТРИКОМПОНЕНТНОЇ СПОЛУКИ $Ba_3CoAl_4O_{10}$ У СИСТЕМІ $BaO-CoO-Al_2O_3$

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Метою даного дослідження було термодинамічне оцінювання імовірності існування трикомпонентної сполуки $Ba_3CoAl_4O_{10}$ у системі $BaO-CoO-Al_2O_3$. Для досягнення поставленої мети розраховано склад трикомпонентної сполуки $Ba_3CoAl_4O_{10}$, що знаходиться на коноді $CoAl_2O_4-Ba_3Al_2O_6$. Здійснено оцінювання температур і складів евтектик у бінарному перетині $CoAl_2O_4-Ba_3Al_2O_6$. У зв'язку з відсутністю літературних даних щодо основних термодинамічних характеристик даної сполуки, розраховано стандартну ентальпію утворення трикомпонентної сполуки, стандартну ентропію і коефіцієнти залежності теплоємності від температури. З використанням методики Бабушкіна, розрахована залежність величини вільної енергії Гіббса від температури для реакцій утворення сполуки $Ba_3CoAl_4O_{10}$. Ймовірність утворення $Ba_3CoAl_4O_{10}$ розраховували як з чистих оксидів барію, кобальту і алюмінію, так і з карбонату барію і оксидів алюмінію та кобальту. Крім того, розрахована ймовірність утворення $Ba_3CoAl_4O_{10}$ із бінарних сполук $CoAl_2O_4$ і $Ba_3Al_2O_6$. Для більш повного аналізу розглядалася ймовірність утворення трикомпонентної сполуки із $Ba_3Al_2O_6$, $BaAl_2O_4$ і CoO, оскільки саме в цьому трикутнику припускається наявність $Ba_3CoAl_4O_{10}$. Побудовані графіки зміни енергії Гіббса у температурному інтервалі 800–2000 К для всіх реакцій. На підставі аналізу отриманих результатів, зроблено висновок, що більш ймовірним з точки зору термодинаміки є утворення трикомпонентної сполуки з оксидів барію, кобальту і алюмінію, аніж з бінарних сполук.

Ключові слова: термодинамічний аналіз, система $BaO-CoO-Al_2O_3$, трикомпонентна сполука $Ba_3CoAl_4O_{10}$, вільна енергія Гіббса, евтектика.

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Keywords: thermodynamic analysis; $BaO-CoO-Al_2O_3$ system; ternary compound $Ba_3CoAl_4O_{10}$; Gibbs energy; eutectic.

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