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STRONTIUM EFFECT ON THE NATURE OF PHASE EQUILIBRIA IN LIQUID METAL CONTAINING CALCIUM AND ALUMINUM

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Abstract. The use of complex strontium-containing alloys with alkaline earth metals for ladle refining of steel allows the efficiency of steel refining and modifying to be improved. Based on binary state diagrams of double systems SrO–CaO, SrO–Al₂O₃, Al₂O₃–CaO and data on the possibility of formation of solid solutions, the state diagram of the SrO–Al₂O₃–CaO system in the temperature range of 1600 – 2600 °C was simulated. Theories of perfect solutions (for solid solutions of strontium and calcium aluminates), regular solutions (for solid oxide solutions) and subregular ionic solutions (for oxide melt) were used to build the liquidus lines. The thermodynamic analysis of the Fe–Sr–Ca–Al–O system as applicable to steel refining processes with calcium and strontium alloys at 1600 °C was carried out. Simulation results show that the complex mechanism of interaction of active elements with oxygen will be implemented in the process of refining steel deoxidized with aluminum. In this case calcium and strontium interaction with oxygen occurs both for elements dissolved in iron, and at the boundary of the gas phase containing calcium and strontium with molten liquid iron. The interaction of calcium and strontium with oxygen in the presence of aluminum (0.05 %) results in a high probability of formation of SrO–Al₂O₃–CaO liquid oxide melts. This greatly facilitates the removal of reaction products from the melt. The resulting non-metallic inclusions are most likely complex calcium and strontium aluminates which are easily assimilated by slag due to the presence of strontium. The formation of undesirable corundum inclusions when treating metal with complex alloys containing strontium and calcium is unlikely.

Keywords: thermodynamics, modeling, phase diagram, strontium, aluminium, calcium

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Оригинальная статья

ВЛИЯНИЕ СТРОНЦИЯ НА ПРИРОДУ ФАЗОВЫХ РАВНОВЕСИЙ В ЖИДКОМ МЕТАЛЛЕ, СОДЕРЖАЩЕМ КАЛЬЦИЙ И АЛЮМИНИЙ

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Аннотация. Применение комплексных стронцийсодержащих сплавов со щелочноземельными металлами для внепечной обработки стали позволяет повысить эффективность процесса рафинирования и модифицирования стали. На основании бинарных диаграмм состояния двойных систем SrO – CaO, SrO – Al₂O₃, Al₂O₃ – CaO и данных о возможности образования твердых растворов смоделирована диаграмма состояния системы SrO – Al₂O₃ – CaO в интервале температур 1600 – 2600 °C. При построении линий ликвидуса для расчета активностей компонентов использованы теории совершенных растворов (для твердых растворов алюминатов стронция и кальция), регулярных растворов (для твердых растворов оксидов) и субрегулярных ионных растворов (для оксидного расплава). Проведен термодинамический анализ системы Fe – Sr – Ca – Al – O применительно к процессам рафинирования стали сплавами с кальцием и стронцием при температуре 1600 °C. Результаты моделирования показали, что в процессе рафинирования стали, раскисленной алюминием, будет реализовываться комплексный механизм взаимодействия активных элементов с кислородом. При этом взаимодействие кальция и стронция с кислородом происходит как для растворенных в железе элементов, так и по границе газовой фазы, содержащей кальций и стронций, с расплавом жидкого железа. В результате взаимодействия кальция и стронция с кислородом в присутствии алюминия (0,05 %) высока вероятность образования жидких оксидных расплавов SrO – Al₂O₃ – CaO, что существенно облегчает удаление продуктов реакции из расплава. Образующиеся неметаллические включения с наибольшей вероятностью являются сложными алюминатами кальция и стронция, которые

благодаря наличию стронция легко ассимилируются шлаком. Образование нежелательных включений корунда при обработке металла комплексными сплавами со стронцием и кальцием маловероятно.

Ключевые слова: термодинамика, моделирование, диаграмма состояния, стронций, алюминий, кальций

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INTRODUCTION

Reducing the contamination of steel with nonmetallic inclusions (NMI) can significantly improve the operational properties of steel products. One of the issues requiring further study is optimization of the processes related to refining of liquid metal in the process of ladle refining of steel. The efficiency and cost-effectiveness of producing critical steel depends primarily on the properties of the materials used, allowing control of the physical and chemical state of the metallic melt [1].

The application of calcium-containing materials for modification helps to control the degree of metal contamination by NMI, as well as the composition and shape of non-metallic inclusions. The use of calcium silicon and ferric calcium in ladle refining is associated with a number of process difficulties. Calcium exhibits a tendency to evaporation and secondary oxidation. This during steel crystallization results in its deficiency and activation of the formation of obstinate refractory calcium aluminates and stringer inclusions of Al_2O_3 . With low and unstable assimilation of calcium by the metal, ensuring the optimal $[\text{Ca}]/[\text{Al}]$ ratio, and, therefore, obtaining confidently high steel quality is a difficult task [2].

At the current time, modifiers containing strontium along with calcium are increasingly being used for refining the metal deoxidized with aluminum. The influence of strontium additives on the processes of liquid steel deoxidation and modification is actively discussed in scientific literature. The application of alloys containing the alkaline earth metals (AEM) complex for processing of 17G1S-U steel helped to improve the purity of the metal in terms of NMI, as well as corrosion resistance and impact strength [3]. The use of strontium-containing modifiers promotes the refinement of both the metal structure and NMI. This results in an increase in the mechanical characteristics of castings [4–6]. Data on the use of strontium as a refining agent is also presented in [7, 8]. Some literature data on phase formation and thermodynamics of elements interaction in liquid iron [15–18] is available for the $\text{Fe}-\text{Al}-\text{Ca}-\text{O}$ [9–12] and $\text{Fe}-\text{Al}-\text{Sr}-\text{O}$ [13, 14] systems. The $\text{Fe}-\text{Sr}-\text{Ca}-\text{Al}-\text{O}$ system, for which thermodynamic parameters are absent in the literature, is also of considerable interest.

The aim of the work is to study thermodynamic analysis of the $\text{Fe}-\text{Sr}-\text{Ca}-\text{Al}-\text{O}$ system during liquid iron

refining with calcium and strontium alloys at a steelmaking temperature of 1600 °C.

SIMULATION METHOD AND RESULTS

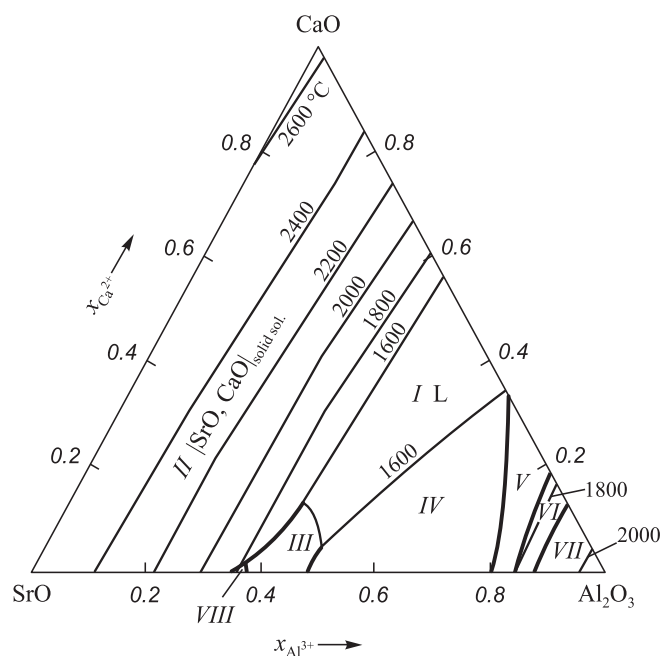
In order to calculate the solubility surface of components in the metal (SSCM) of the $\text{Fe}-\text{Sr}-\text{Ca}-\text{Al}-\text{O}$ system, thermodynamic data on the triple state diagram of the $\text{SrO}-\text{Al}_2\text{O}_3-\text{CaO}$ oxide system is required. In [17], the state diagram with only schematic division is given. The presence of solid solutions: calcium and strontium oxides and aluminates is shown. In [18] a calculated state diagram of this system was built on the basis of [17].

In this work, binary diagrams of the $\text{SrO}-\text{CaO}$ [19], $\text{SrO}-\text{Al}_2\text{O}_3$ [20] and $\text{Al}_2\text{O}_3-\text{CaO}$ [21] state and data on the possibility of formation of solid solutions [17] were used to simulate the state diagram of the $\text{SrO}-\text{Al}_2\text{O}_3-\text{CaO}$ system in the temperature range of 1600–2600 °C. Theories of perfect solutions (for solid solutions of strontium and calcium aluminates), regular solutions (for solid oxide solutions) and subregular ionic solutions (for oxide melt) were used to build the liquidus lines.

This paper presents the calculated state diagram (Fig. 1) of the $\text{SrO}-\text{Al}_2\text{O}_3-\text{CaO}$ system. The diagram consists of eight stability areas of the following phases: *I* is the area of liquid oxides (SrO , Al_2O_3 , CaO); *II* is the area of solid solution of $|\text{SrO}, \text{CaO}|$ with unlimited solubility in each other; *III* is the area of solid solution of $(\text{Sr}, \text{Ca})_3\text{Al}_2\text{O}_6$ based on strontium aluminate; *IV*, *V* and *VI* are the areas of solid solutions of strontium and calcium mono-, bi- and hexaaluminates; *VII* is the area of corundum; and *VIII* is the area of $\text{Sr}_4\text{Al}_2\text{O}_7$. No ternary compounds were detected in the system in question. Wide areas of solid solutions (oxides and various calcium and strontium aluminates) can be seen in the diagram.

In Table 1 (*K* is a melt constant of oxides and their compounds) thermodynamic data are given, used to calculate the state diagram of the $\text{SrO}-\text{Al}_2\text{O}_3-\text{CaO}$ system. Straight brackets in this table correspond to solid oxides and compounds, and parentheses correspond to oxide melt components.

The theory of subregular ionic solutions, taking into account the dependence of the coordination number on the slag composition, and the method of selecting the energy parameters for an oxide melt are described

Fig. 1. Calculated diagram of the SrO – Al₂O₃ – CaO systemРис. 1. Расчетная диаграмма состояния системы SrO – Al₂O₃ – CaO

in [21]. Table 2 shows the energy parameters of the theory of subregular ionic solutions for the SrO–Al₂O₃–CaO oxide system. The activities of the SrO–CaO solid solution components were calculated using the theory of regular solutions [21] (the energy parameter of the theory is 28,568 J/mol [19]). The activities of strontium and calcium aluminate solid solutions components were equated to their mole fractions [21].

When considering the interaction of calcium, strontium, and aluminum with oxygen in liquid iron, double

Table 1

Thermodynamic data for phase transition reactions

Таблица 1. Термодинамические данные для реакций фазовых превращений

Reaction	$\lg K = -A/T + B$		Source
	A	B	
$ \text{SrO} = (\text{SrO})$	4229	1.507	[19]
$ \text{Al}_2\text{O}_3 = (\text{Al}_2\text{O}_3)$	5683	2.447	[22]
$ \text{CaO} = (\text{CaO})$	2732	0.945	[19]
$ \text{Sr}_4\text{Al}_2\text{O}_7 = 4(\text{SrO}) + (\text{Al}_2\text{O}_3)$	9023	–0.908	[20]
$ \text{Sr}_3\text{Al}_2\text{O}_6 = 3(\text{SrO}) + (\text{Al}_2\text{O}_3)$	11,797	1.020	[20]
$ \text{Ca}_3\text{Al}_2\text{O}_6 = 3(\text{CaO}) + (\text{Al}_2\text{O}_3)$	10,260	1.570	[21]
$ \text{SrAl}_2\text{O}_4 = (\text{SrO}) + (\text{Al}_2\text{O}_3)$	9101	1.533	[20]
$ \text{CaAl}_2\text{O}_4 = (\text{CaO}) + (\text{Al}_2\text{O}_3)$	5507	0.482	[21]
$ \text{SrAl}_4\text{O}_7 = (\text{SrO}) + 2(\text{Al}_2\text{O}_3)$	7653	0.449	[20]
$ \text{CaAl}_4\text{O}_7 = (\text{CaO}) + 2(\text{Al}_2\text{O}_3)$	13,661	3.726	[21]
$ \text{SrAl}_{12}\text{O}_{19} = (\text{SrO}) + 6(\text{Al}_2\text{O}_3)$	16,523	3.546	[20]
$ \text{CaAl}_{12}\text{O}_{19} = (\text{SrO}) + 6(\text{Al}_2\text{O}_3)$	44,787	17.285	[21]

and triple oxide state diagrams (Table 2) need to be considered. However, the main diagram determining the non-metallic inclusions in the system under consideration will be the SrO–Al₂O₃–CaO diagram (Fig. 1).

Table 3 shows all possible reactions which can occur in the Fe–Sr–Ca–Al–O system. However, only some reactions are possible depending on the composition of the liquid metal, temperature and total pressure.

Table 2

Parameters of the theory of subregular ionic solutions (FeO, SrO, CaO, Al₂O₃)

Таблица 2. Параметры теории субрегулярных ионных растворов (FeO, SrO, CaO, Al₂O₃)

System	Energy parameters, J/mol			Source
FeO – SrO	–71,828	–22,026	–20,905	[19]
FeO – CaO	–25,767	–56,788	–26,522	[23]
FeO – Al ₂ O ₃	+212	–21,502	–11,091	[25]
SrO – CaO	–22,505	–35,041	–27,933	[19]
SrO – Al ₂ O ₃	–104,349	–217,689	–104,436	[20]
CaO – Al ₂ O ₃	–51,474	–172,657	–97,668	[23]
FeO – SrO – CaO	–139,162	–90,793	–101,819	[19]
FeO – SrO – Al ₂ O ₃	–200,000	–253,200	–263,800	[24]
FeO – CaO – Al ₂ O ₃	–145,150	–200,814	–233,108	[23]
SrO – CaO – Al ₂ O ₃	–234,938	–185,780	–367,940	this work

Square brackets in the table correspond to metallic melt, curved brackets correspond to the gas phase, and parentheses and straight brackets correspond to oxide and metallic melts. Temperature dependences of the equilibrium constant of chemical reactions taking place in the system under study are also given.

Strontium and calcium oxides form a continuous series of solid solutions [19], and iron oxide FeO dissolves only in oxide CaO (not more than 0.05 at 1600 °C). For the FeO in CaO solution, the energy parameter of the theory of regular solutions is 33,362 J/mol.

Table 4 lists the first-order interaction parameters required to calculate the activity of metallic melt components.

Projection of the solubility surface on the plane can be built only for two components (oxygen content is given by iso-oxygen sections), therefore, one of the components of the metal melt in the Fe–Sr–Ca–Al–O system shall be recorded. In this work we performed calculations for two variants: the aluminum (Fig. 2)

or calcium (Fig. 3) concentration is recorded at a temperature of 1600 °C; and the total pressure of 101.3 and 202.6 kPa (dashed and dash-dotted lines). When calculating the Fe–Sr–Ca–Al–O–C system, carbon content must also be recorded (Fig. 4, 5). The final composition of the metal after the completion of the refining process is plotted on the solubility surface of components in the metal (SSCM). The thin lines are iso-oxygen sections of the solubility surface. The contrasting lines show compositions of the liquid metal in equilibrium with two oxide phases. The areas bounded by contrasting lines show compositions of liquid metal in equilibrium with one oxide phase. Area *I* shows the compositions of liquid metal in equilibrium with oxide melt (OM); *II* – with solid oxide solutions; *III* – with solid solution (Sr, Ca)₃Al₂O₆ based on strontium aluminate; *IV*, *V* and *VI* – with solid solutions of strontium and calcium mono-, bi- and hexaaluminates; *VII* – with corundum; *IX* – with the gas phase {Sr, Ca}; *X* – with the gas phase {Sr, Ca, CO, CO₂} with traces of CO, CO₂; *XI* – with the gas phase {Sr, Ca, CO, CO₂} of variable composi-

Table 3

Temperature dependences of equilibrium constants of chemical reactions in the metal melt of the Fe–Al–Sr–Ca–O–C system

Таблица 3. Температурные зависимости константы равновесия химических реакций, протекающих в металлическом расплаве системы Fe–Al–Sr–Ca–O–C

Chemical reaction	$\lg K = -A/T + B$	Source
$(\text{FeO}) = [\text{Fe}] + [\text{O}]$	$-6320/T + 4.734$	[21]
$(\text{SrO}) = [\text{Sr}] + [\text{O}]$	$-25,5719/T + 9.493$	[19]
$(\text{CaO}) = [\text{Ca}] + [\text{O}]$	$-31,368/T + 12.515$	[23]
$(\text{Al}_2\text{O}_3) = 2[\text{Al}] + 3[\text{O}]$	$-58,383/T + 18.063$	[23]
$ \text{SrO} _{\text{solid sol.}} = [\text{Sr}] + [\text{O}]$	$-29,800/T + 11.000$	[19]
$ \text{CaO} _{\text{solid sol.}} = [\text{Ca}] + [\text{O}]$	$-34,100/T + 13.460$	[23]
$ \text{FeO} _{\text{solid sol.}} = [\text{Fe}] + [\text{O}]$	$-8069/T + 5.800$	[21]
$ \text{Al}_2\text{O}_3 = 2[\text{Al}] + 3[\text{O}]$	$-64,000/T + 20.480$	[23]
$ \text{Sr}_3\text{Al}_2\text{O}_6 _{\text{solid sol.}} = 3[\text{Sr}] + 2[\text{Al}] + 6[\text{O}]$	$-146,893/T + 47.562$	[20]
$ \text{Ca}_3\text{Al}_2\text{O}_6 _{\text{solid sol.}} = 3[\text{Sr}] + 2[\text{Al}] + 6[\text{O}]$	$162,747/T + 48.112$	[21]
$ \text{SrAl}_2\text{O}_4 _{\text{solid sol.}} = [\text{Sr}] + 2[\text{Al}] + 4[\text{O}]$	$-93,055/T + 29.089$	[20]
$ \text{CaAl}_2\text{O}_4 _{\text{solid sol.}} = [\text{Ca}] + 2[\text{Al}] + 4[\text{O}]$	$-95,258/T + 31.064$	[21]
$ \text{SrAl}_4\text{O}_7 _{\text{solid sol.}} = [\text{Sr}] + 4[\text{Al}] + 7[\text{O}]$	$-149,990/T + 46.068$	[24]
$ \text{CaAl}_4\text{O}_7 _{\text{solid sol.}} = [\text{Ca}] + 4[\text{Al}] + 7[\text{O}]$	$-161,795/T + 52.367$	[21]
$ \text{SrAl}_{12}\text{O}_{19} _{\text{solid sol.}} = [\text{Sr}] + 12[\text{Al}] + 19[\text{O}]$	$-398,189/T + 124.493$	[24]
$ \text{CaAl}_{12}\text{O}_{19} _{\text{solid sol.}} = [\text{Ca}] + 12[\text{Al}] + 19[\text{O}]$	$-426,453/T + 138.178$	[21]
$\{\text{Sr}\} = [\text{Sr}]$	$1870/T - 3.650$	[19]
$\{\text{Ca}\} = [\text{Ca}]$	$1912/T - 2.690$	[23]
$\{\text{CO}\} = [\text{C}] + [\text{O}]$	$-1168/T - 2.070$	[26]
$\{\text{CO}_2\} = [\text{C}] + 2[\text{O}]$	$-9616/T + 2.510$	[26]

Table 4

Parameters of interaction of liquid iron components e_i^j at 1600 °C

Таблица 4. Параметры взаимодействия компонентов жидкого железа e_i^j при температуре 1600 °C

$i \backslash j$	Sr	Al	Ca	O	C
Sr	0 [19]	0 [24]	0 [19]	-3.94 [19]	0 [19]
Al	0 [24]	0.045 [28]	-0.047 [27]	-1.98 [28]	0.091 [27]
Ca	0 [19]	-0.072 [27]	-0.002 [27]	-3.62 [19]	-0.340 [27]
O	-0.72 [19]	-1.170 [28]	-1.410 [29]	-0.20 [27]	-0.450 [27]
C	0 [19]	0.043 [27]	-0.097 [27]	-0.34 [27]	0.140 [27]

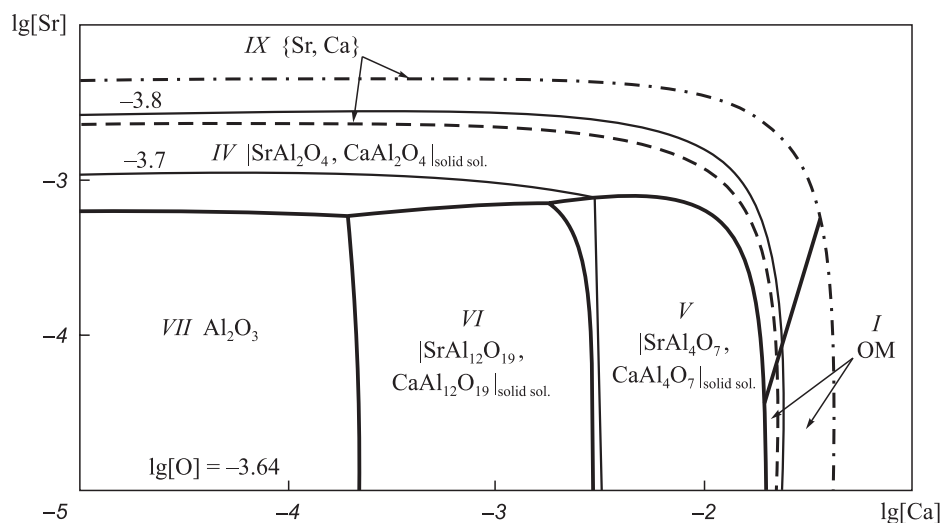


Fig. 2. SSCM of the Fe–Sr–Ca–Al–O system ($t = 1600$ °C, $[Al] = 0.05$ %)

Рис. 2. ПРКМ системы Fe–Sr–Ca–Al–O ($t = 1600$ °C, $[Al] = 0,05$ %)

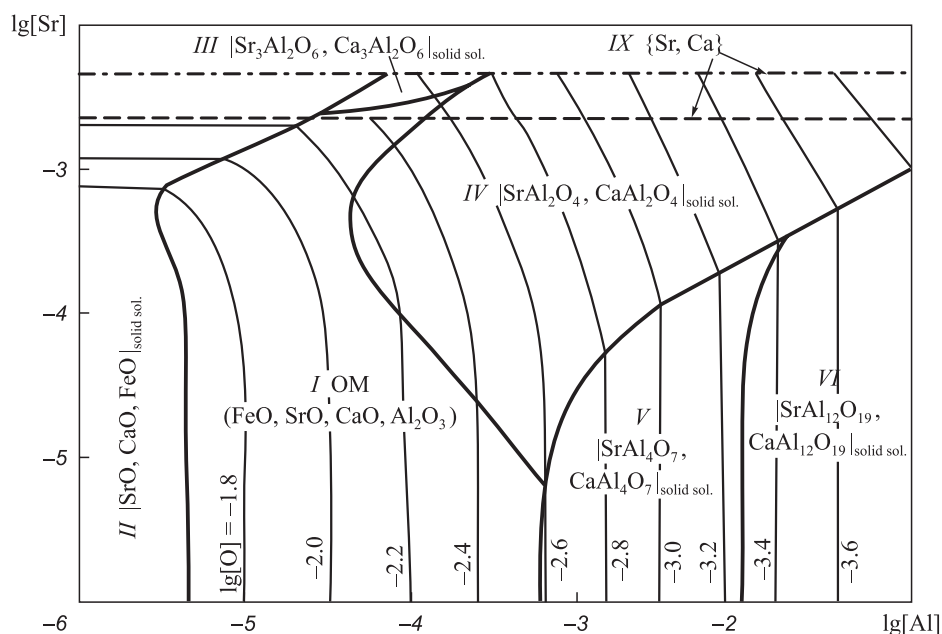


Fig. 3. SSCM of the Fe–Sr–Ca–Al–O system ($t = 1600$ °C, $[Ca] = 0.001$ %)

Рис. 3. ПРКМ системы Fe–Sr–Ca–Al–O ($t = 1600$ °C, $[Ca] = 0,001$ %)

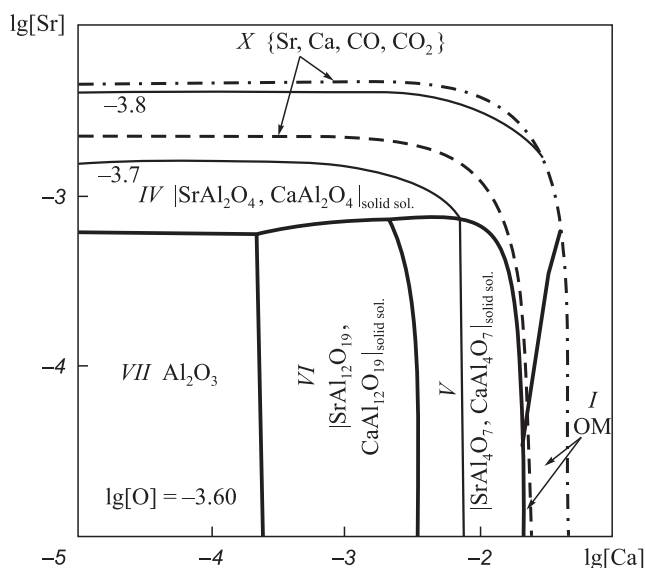


Fig. 4. SSCM of the Fe–Sr–Ca–Al–O–C system ($t = 1600\text{ }^{\circ}\text{C}$, $[\text{Al}] = 0.05$, $[\text{C}] = 0.1\text{ }\%$)

Рис. 4. ППКМ системы Fe–Sr–Ca–Al–O–C ($t = 1600\text{ }^{\circ}\text{C}$, $[\text{Al}] = 0,05\text{ }\%$, $[\text{C}] = 0,1\text{ }\%$)

tion. All numbers of areas in Fig. 1 (except *VIII*) and in Fig. 2–5 correspond to each other. Area *VIII* in Fig. 2–5 is absent, since this area should be marked with compositions of metal in equilibrium with $\text{Sr}_4\text{Al}_2\text{O}_7$. However, its formation at given calcium or aluminum concentrations and temperature of $1600\text{ }^{\circ}\text{C}$ is unlikely.

In Fig. 2–4 and 5, *b* the gas phase area is projected onto a line, as it is located perpendicular to the plane of the figures. In Fig. 5, *a* (202.6 kPa) the area of liquid metal compositions in equilibrium with the gas phase is quite wide. Table 5 shows the contents of strontium, aluminum and oxygen in liquid iron and their corresponding partial pressures $\{\text{Sr}, \text{Ca}, \text{CO}, \text{CO}_2\}$. It can be seen that composition of the gas phase varies from 96.24 kPa for CO to 96.24 kPa for strontium. At the same time, the calcium pressure in the gas mixture remains almost constant (approximately 4.05 kPa), regardless of the strontium and aluminum concentrations.

The formation of aluminate solid solution based on $\text{Sr}_3\text{Al}_2\text{O}_6$ (area *III*) is possible only at elevated pressure (above 1 atm) and strontium concentrations above $0.003\text{ }\%$ (hereinafter by weight) in the Fe–Sr–Ca–Al–O system (Fig. 3). In the presence of minimum carbon concentrations ($0.1\text{ }\%$) in the system under study, it is also the solid solution under study (Fig. 5, *a*) cannot be formed at atmospheric pressure but possible at increased pressure (Fig. 5, *b*).

Calcium monoaluminate has a melting point of $1601\text{ }^{\circ}\text{C}$ [21], so in practice it does not represent non-metallic inclusions. However, in the presence of strontium, it appears on the SSCM of the Fe–Sr–Ca–Al–O system (Fig. 2–5) as a solid solution with strontium

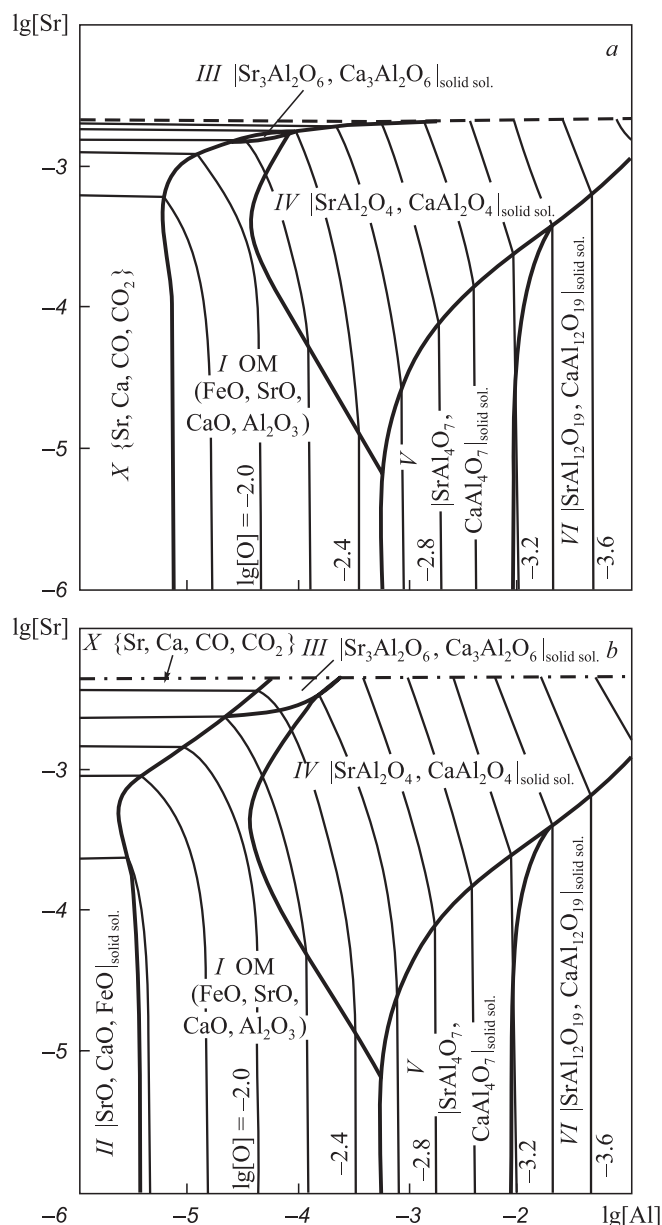


Fig. 5. SSCM of the Fe–Sr–Ca–Al–O–C system ($t = 1600\text{ }^{\circ}\text{C}$, $[\text{Ca}] = 0.001$, $[\text{C}] = 0.1\text{ }\%$ and $P_{\text{tot}} = 1$ (a) and 2 atm (b))

Рис. 5. ППКМ системы Fe–Sr–Ca–Al–O–C ($t = 1600\text{ }^{\circ}\text{C}$, $[\text{Ca}] = 0,001\text{ }\%$, $[\text{C}] = 0,1\text{ }\%$ и $P_{\text{общ}} = 1$ (a) и 2 атм (b))

aluminate. According to the calculations, the formation of strontium and calcium mono- and bialuminates is most likely.

The possibility of formation of liquid oxide inclusions deep in the metal (pressure over 101.3 kPa) is very likely. This allows prediction of high refining properties of complex alloys with calcium and strontium in the metal deoxidized with aluminum.

CONCLUSION

In the process of refining steel deoxidized with aluminum, the complex mechanism of interaction of the

Table 5

Composition of liquid metal and gas phase (Fig. 5, a, [Ca] = 0.001 %)

Таблица 5. Состав жидкого металла и газовой фазы (рис. 5, а, [Ca] = 0,001 %)

Composition of metal			Composition of gas phase, atm			
lg[Sr, %]	lg[Al, %]	lg[O, %]	$P_{\{CO\}}$	$P_{\{CO_2\}}$	$P_{\{Sr\}}$	$P_{\{Ca\}}$
–5.00	–5.15	–1.68	0.945	0.015	0.004	0.036
–3.00	–5.12	–1.90	0.550	0.050	0.401	0.039
–2.92	–5.00	–1.98	0.474	0.004	0.482	0.040
–2.80	–4.50	–2.20	0.286	0.001	0.672	0.041
–2.69	–3.00	–2.94	0.053	Under 10^{-5}	0.904	0.043
–2.67	–1.00	–3.83	0.005	Under 10^{-5}	0.953	0.042

active elements with oxygen is likely. Calcium and strontium interaction with oxygen occurs both for elements dissolved in iron and at the boundary of the gas phase containing calcium and strontium with the liquid iron melt. The interaction of calcium and strontium with oxygen with the aluminum content typical for industrial technologies may result in the formation of liquid oxide melts $SrO-Al_2O_3-CaO$. This greatly facilitates the removal of reaction products from the melt. The NMI thus

formed are most likely complex calcium and strontium aluminates, which are easily removed from the melt due to the presence of strontium. The formation of undesirable corundum Al_2O_3 inclusions when treating metal with complex alloys with strontium and calcium is unlikely. The thermodynamic analysis of processing steel deoxidized with aluminum by complex alloys containing calcium and strontium allows predicting the high refining capacity of such alloys.

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