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Direct Microalloying of Steel with Cerium under Slags of $CaO-SiO_2-Ce_2O_3$–15% Al_2O_3–8% MgO System with Additional Reducing Agents

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Abstract—An assessment of the possibility of steel direct microalloying with cerium was performed using thermodynamic modeling of cerium reduction from slags of $CaO-SiO_2-Ce_2O_3$ system containing 15% Al_2O_3 and 8% MgO, additional additives of reducing agents (aluminum or ferrosilicon-aluminum), at temperatures of 1550 and 1650°C using the HSC 6.1 Chemistry (Outokumpu) software package. Depending on the additional additives of aluminum or ferrosilicon-aluminum, metal temperature, slag basicity and content of cerium oxide, 0.228 to 40.5 ppm of cerium transfers into the metal. With an additional additive of aluminum from slag (Y_1) containing 1.0% of cerium oxide, 0.228 ppm of cerium is transferred to the metal at 1550°C. An increase in the system temperature to 1650°C is accompanied by a slight increase in cerium content, reaching no more than 0.323 ppm. When added to ferrosilicon-aluminum metal, cerium content in the metal is higher and amounts to 0.402 and 0.566 ppm at 1550 and 1650°C, respectively. When concentration of cerium oxide in the slag (Y_2) increases to 7.0%, more significant increase in cerium content in the metal is observed, reaching in temperature range of 1550–1650°C, 1.65–2.31 ppm with aluminum additives and 2.90–4.05 ppm with ferrosilicon-aluminum additives. The most noticeable increase in cerium content in the metal is observed with an increase in slag basicity. During formation of slags with basicity of 2–3, containing 1–7% Ce_2O_3, the equilibrium concentration of cerium in the metal varies from 0.5 to 4 ppm with aluminum additives and 1–7 ppm with ferrosilicon-aluminum additives at 1550°C. Slags transfer to the increased (up to 3–5) basicity is accompanied by an increase in the equilibrium content of cerium in the metal to 4–12 ppm with aluminum additives and 7–20 ppm with ferrosilicon-aluminum additives at Ce_2O_3 content of 3–7% and, as a result, an increase in efficiency of cerium reduction process.

Keywords: steel, cerium, slag, basicity, cerium oxide, phase composition, experiment planning, thermodynamic modeling

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INTRODUCTION

Due to the increase in the length of gas transmission pipelines on Russian territory, investigations and development of pipe steels with a set of high mechanical characteristics become more and more relevant. Microalloying of steel with rare-earth metals (REMs) is one of the directions of the solution of the problem of production of high-strength pipe steels. Microalloying of steel with REMs provides a desired set of mechanical characteristics [1–5].

A positive effect of REMs on the strength, ductility, impact strength, and resistance to cyclic delamination of 17G1S pipe steel is particularly indicated. It was shown that high resistance to general and pitting corrosion, as well as sulfide stressed-corrosive failure of low-alloyed steels and weld joints can be achieved through microalloying of REM steel [3]. The service life of pipes from 17G1S steel with REM increases at the growth stage of fatigue cracks due to the increase in the toughness at cyclic failure of steel. According to the data from [4], the brittle fracture increased remarkably as a result of modification of 17G1S steel with 0.01–0.06% cerium and the optimal relationship between brittle fracture and reserve of toughness was achieved. Introduction of cerium and lanthanum to the low-carbon steel provides the formation of fine-

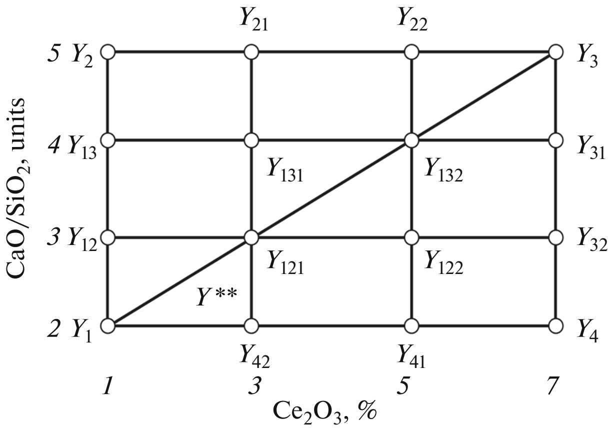

Fig. 1. Area of variation of the slag composition of the local simplex.

grained structure, because REMs form nonmetallic inclusions in the molten steel, which represent heterogeneous nucleation centers during solidification [5].

Microalloying of steel with REMs is usually carried out using additives of ferroalloys, employment of which increases the cost of steel. Microalloying of steel with REMs through their reduction from the oxide systems is one of the directions of solution of the problem of cost. In addition, a positive effect of Ce_2O_3 on physicochemical and refining properties of CaO–Al_2O_3–SiO_2 slags and structure and mechanical properties of the produced metal is indicated [6–15].

One example is that the addition of Ce_2O_3 to slag decreases the activity of Al_2O_3 due to the formation of $Ce_2O_3 \cdot Al_2O_3$ compound [6] and thus increases the absorption ability of Al_2O_3 inclusions with refining slag [9]. It was shown that the melting point and toughness of slag decrease with an increase in the amount of Ce_2O_3 additives with the CaO-to-Al_2O_3 mass ratio of 1.57. The toughness range of the CaO–Al_2O_3–SiO_2–Ce_2O_3 slag system is from 0.289 to 0.497 Pa s at 1500°C [7]. Microstructure of the melted metal with the addition of REM oxides to the slag is dispersed and consists of ferrite and a low amount of perlite. The obtained metal is characterized by the lowest (5–10 μm) grain size with the addition of 5.94 wt % of REM oxide to slag [8].

Addition of rare-earth metal oxides to CaO–SiO_2 slags is effective for the increase in the sulfide capacity. One example is that addition of 1.83 mol % Ce_2O_3 increases the sulfide capacity by ca. 50% for the slag with the basicity of 1.22 [10].

In addition, the possibility of cerium reduction from the slag of the oxide system under study and cerium dissolution in steel at the amount of 6 ppb is indicated, which represented microalloying effect in steel and modification of Al_2O_3 inclusion [11]. Thermodynamic analysis showed that inclusions of $Ce_2O_3 \cdot Al_2O_3$ type will be formed at the cerium content of 6.7 ppb to 3.6 ppm, when the aluminum content is 0.01 wt % [12]. In [16, 17], the fundamental possibility of the development of the reduction of cerium from slags of the CaO–SiO_2–Ce_2O_3–15% Al_2O_3–8% MgO system with aluminum dissolved in metal was confirmed. It was shown that 0.055 to 16.0 ppm cerium is transferred to the steel containing 0.06% C, 0.25% Si, and 0.05% Al depending on the temperature of metal, basicity of slag, and content of cerium oxide.

In this work, the possibility and completeness of reduction of cerium from the slags of the CaO–SiO_2–Ce_2O_3–15% Al_2O_3–8% MgO system by additional additives of aluminum or ferrosilicon-aluminum to metal at the temperature values of 1550 and 1650°C were evaluated using the results of thermodynamic modeling.

PROCEDURE OF MODELING

Evaluation of the possibility of direct microalloying of steel with cerium was carried out using thermodynamic modeling of the reduction of cerium from the slags of the CaO–SiO_2–Ce_2O_3 system containing 15% Al_2O_3 and 8% MgO with additional additives of aluminum or ferrosilicon-aluminum at the temperature values of 1550 and 1650°C. The HSC 6.1 Chemistry program complex (Outokumpu) was used, which is based on minimization of the Gibbs energy and variation principles of thermodynamics [16–18], and the method of simplex planning lattices was employed [19, 20]. During generation of the planning matrix, the following restrictions were imposed on variable components of the CaO–SiO_2–Ce_2O_3–Al_2O_3–MgO system: CaO-to-SiO_2 ratio is 2–5, 15% Al_2O_3, 8% MgO, and 1–7% Ce_2O_3. As a result of imposed restrictions on the variation of the components in the system, the range under study is represented by the local simplex in the form of two concentration triangles, tops of which are represented by pseudo-components Y_1, Y_2, Y_3, and Y_4 (Fig. 1).

Thermodynamic modeling was carried out for the working mass of solid of 100 kg (90% of metal and 10% of slag) under the ambient air pressure of 0.1 MPa. Chemical composition of slag at the points of local simplex and results of modeling of the equilibrium cerium content in metal containing 0.06% C, 0.25% Si, and 0.05% Al are given in Table 1. Additives of secondary aluminum or ferrosilicon-aluminum were added to the metal at amounts, which provide the concentration of aluminum of 0.15 and 0.20% in metal, respectively.

RESULTS AND DISCUSSION

Results of thermodynamic modeling of reduction of cerium from the slags of the CaO–SiO_2–Ce_2O_3 system containing 15% Al_2O_3 and 8% MgO are given in

Table 1. Chemical composition of the slag at the local simplex points and results of thermodynamic modeling of cerium equilibrium content in the metal

No.	Slag index	Chemical composition of slag, wt %					Cerium content, ppm, at temperature, °C			
							aluminum additive		ferrosilicon-aluminum additive	
		CaO	SiO_2	Al_2O_3	MgO	Ce_2O_3	1550	1650	1550	1650
1	pY_1	50.7	25.3	15.0	8.0	1.0	0.228	0.323	0.402	0.566
2	Y_2	63.3	12.7	15.0	8.0	1.0	2.920	4.060	4.960	6.900
3	Y_3	58.3	11.7	15.0	8.0	7.0	17.700	24.000	29.900	40.500
4	Y_4	46.7	23.3	15.0	8.0	7.0	1.650	2.310	2.900	4.050
5	Y_{13}	59.1	16.9	15.0	8.0	1.0	1.320	1.850	2.260	3.1600
6	Y_{132}	56.0	16.0	15.0	8.0	5.0	6.310	8.740	10.800	14.90
7	Y_{22}	60.0	12.0	15.0	8.0	5.0	13.300	18.200	22.500	30.700
8	Y_{12}	54.9	21.1	15.0	8.0	1.0	0.586	0.823	1.010	1.410
9	Y_{121}	53.2	20.8	15.0	8.0	3.0	1.660	2.320	2.870	3.990
10	Y_{21}	61.6	12.4	15.0	8.0	3.0	8.260	11.400	14.000	19.300
11	Y_{131}	57.5	16.5	15.0	8.0	3.0	3.840	5.340	6.5600	9.100
12	Y_{41}	48.0	24.0	15.0	8.0	5.0	1.150	1.630	2.04	2.850
13	Y_{31}	54.5	15.5	15.0	8.0	7.0	8.730	12.000	14.900	20.400
14	Y_{42}	49.4	24.6	15.0	8.0	3.0	0.698	0.985	1.230	1.720
15	Y_{32}	50.5	19.5	15.0	8.0	7.0	3.970	5.530	6.860	9.490
16	Y_{122}	51.9	20.1	15.0	8.0	5.0	2.830	3.950	4.890	6.780

Table 1 in the form of composition–property (equilibrium content of cerium in metal) diagrams at the temperature values of 1550 and 1650°C with aluminum additives (Fig. 2) and ferrosilicon-aluminum additives (Fig. 3) (isolines of the equilibrium cerium content are indicated as blue lines in the diagrams, while thin black lines indicate the basicity of slag (B = CaO-to-SiO_2), and digits indicate their magnitudes). Analysis of the diagrams provides a quantitative evaluation of the effect of temperature of metal and chemical composition of slag on the cerium content.

Depending on additives of reducing agents (aluminum or ferrosilicon-aluminum), temperature of metal, basicity of slag, and the ceria content, from 0.228 to 40.5 ppm cerium, is transferred to metal (Table 1). With an additional additive of aluminum, a total of 0.228 ppm of cerium is transferred to metal at the temperature of 1550°C from the slag (Y_1) containing 1.0% of ceria. An increase in the temperature of the system to 1650°C is accompanied by the marginal increase in the concentration of cerium amounting to less than 0.323 ppm. During addition of ferrosilicon-aluminum to metal, the cerium content in the metal is higher and corresponds to 0.402 and 0.566 ppm at the temperature of 1550 and 1650°C, respectively. With an increase in the concentration of ceria in slag (Y_2) to 7.0%, a more remarkable increase in the cerium content in the metal is observed, which amounts to 1.65–2.31 ppm in the temperature range of 1550–1650°C using aluminum additives and 2.9–4.05 ppm using ferrosilicon-aluminum additives.

The most notable increase in the cerium content in metal is observed with an increase in the slag basicity. During the formation of slags containing 1–7%

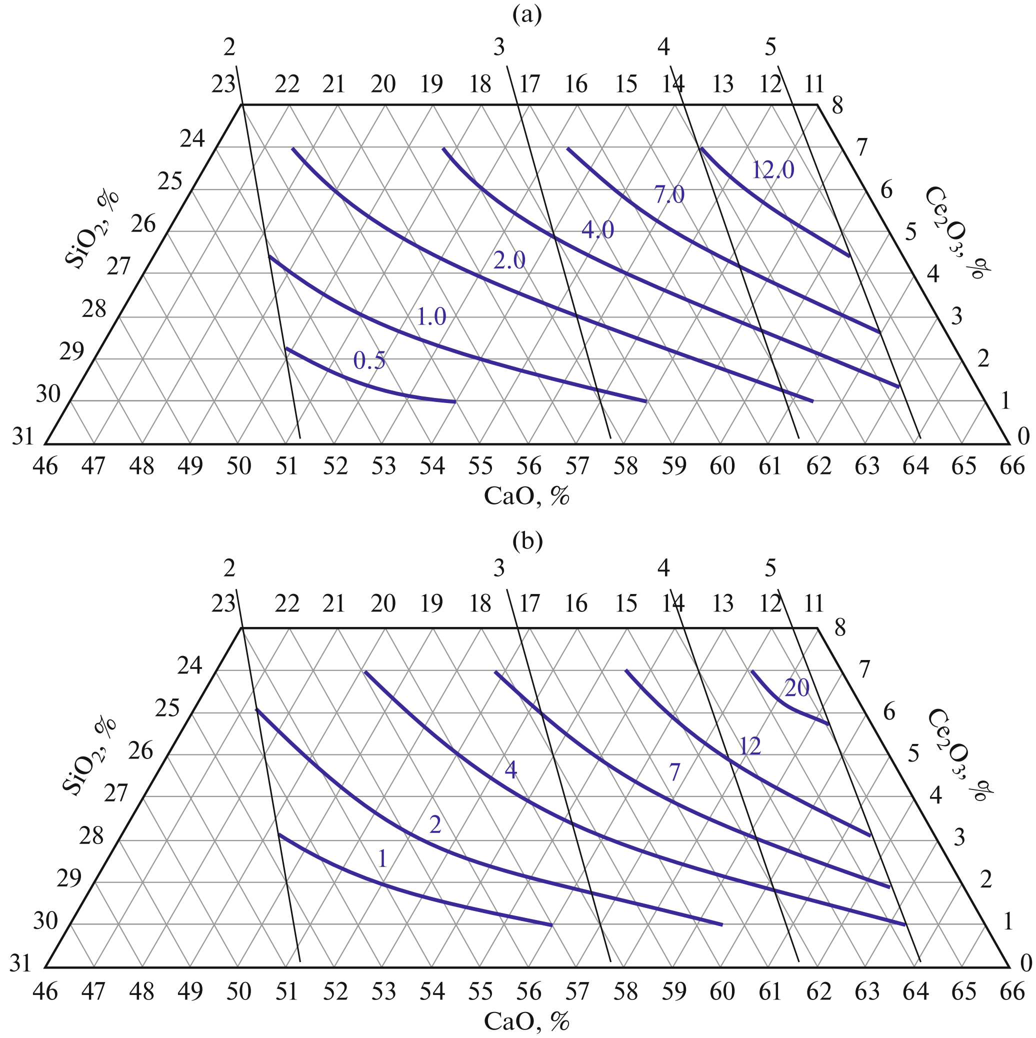

Fig. 2. Diagram of cerium equilibrium content in the metal held under the slag of $CaO–SiO_2–Ce_2O_3$ system containing 15% Al_2O_3 and 8% MgO at temperatures of (a) 1550°C and (b) 1650°C with an aluminum additive.

Ce_2O_3, the equilibrium concentration of cerium in metal in the basicity range of 2–3 varies from 0.5 to 4 ppm using aluminum additives (Fig. 2a) and 1–7 ppm using ferrosilicon-aluminum additives (Fig. 3a) at 1550°C. The shift of the slags to the range of higher basicity (3–5) is accompanied by the increase in the equilibrium concentration of cerium in metal up to 4–12 ppm at the content of 3–7% Ce_2O_3 using aluminum additives and 7–20 ppm using additives of ferrosilicon-aluminum and, consequently, an increase in the effectiveness of the reduction of cerium. At the temperature of 1650°C, the equilibrium concentration of cerium in metal in the basicity range of 2–3 and the content of 1–7% Ce_2O_3 varies in the range of 1–7 ppm using aluminum additives (Fig. 2b) and 1–12 ppm using ferrosilicon-aluminum additives (Fig. 3b). The shift of the slags to the increased basicity (3–5) is accompanied by the increase in the equilibrium concentration of cerium in metal up to 4–20 ppm at the content of 3–7% Ce_2O_3 using aluminum additives and 7–30 ppm using ferrosilicon-aluminum additives.

A positive effect of the temperature factor, basicity of the formed slags, and the content of ceria in the studied range of chemical composition on the reduction of cerium was fundamentally rationalized by the features of phase composition of the formed slags and thermodynamics of chemical reactions of reduction of cerium with aluminum dissolved in metal [16, 17].

CONCLUSIONS

It has been determined that from 0.228 to 40.5 ppm of cerium is transferred into the steel containing 0.06% of carbon, 0.25% of silicon, and 0.05% of aluminum depending on the temperature of metal, basicity of slag, and the content of ceria using additional additives

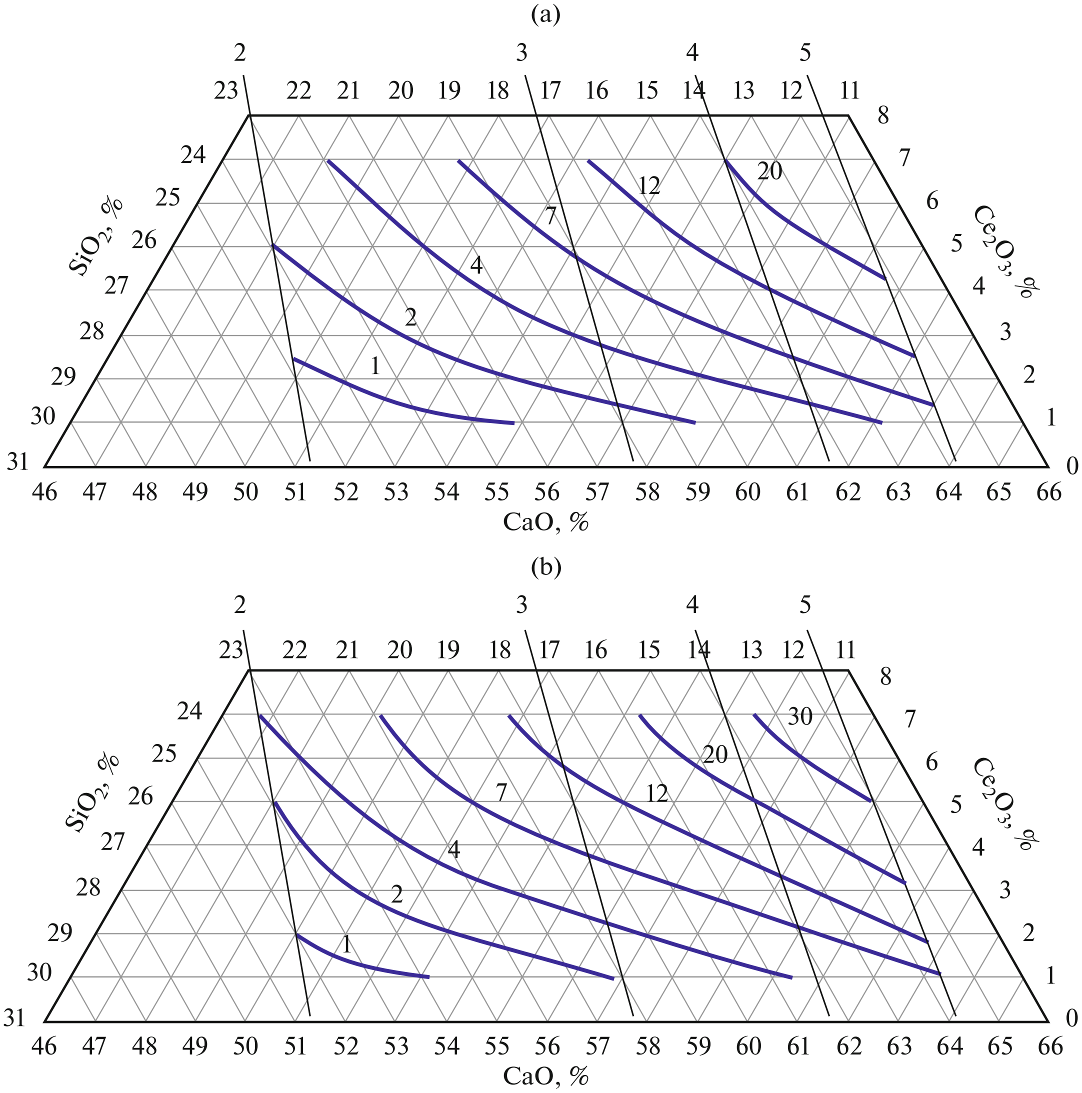

Fig. 3. Diagram of cerium equilibrium content in the metal held under the slag of $CaO-SiO_2-Ce_2O_3$ system containing 15% Al_2O_3 and 8% MgO at temperatures of (a) 1550°C and (b) 1650°C with ferrosilicon-aluminum additive.

of secondary aluminum or ferrosilicon-aluminum, which provide the concentration of aluminum in metal of 0.15 and 0.20%, respectively. A positive effect of the temperature factor, basicity of slags, and the content of ceria in the studied range of chemical composition on the reduction of cerium is caused by the features of phase composition of the formed slags and thermodynamics of cerium reduction.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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