Study of possibility of cerium reduction from slags of CaO-SiO$_2$-Ce$_2$O$_3$–15%Al$_2$O$_3$–8%MgO system

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Abstract. By means of theoretical and experimental studies it is shown that it is possible to reduction cerium from the slags of the CaO–SiO$_2$–Ce$_2$O$_3$ system containing 15%Al$_2$O$_3$ and 8 % MgO, by aluminum dissolved in metal, at temperatures of 1550 and 1650°C. The results of mathematical modeling are presented graphically as ‘composition – equilibrium content of cerium in metal’ diagrams. It is found that depending on temperature of metal, basicity of slag and the content of cerium oxide, from 0.055 to 16 ppm cerium passes into metal containing 0.06 % of carbon, 0.25 % of silicon and 0.055 % of aluminium. Positive influence of the temperature factor, basicity of slags and the content of cerium oxide in a studied range of chemical composition on process of cerium reduction is explained from the perspective of phase structure of formed slags and thermodynamics of reactions of cerium reduction. The possibility of reduction of cerium from slags of CaO–SiO$_2$–Ce$_2$O$_3$ system, containing 15 % Al$_2$O$_3$ and 8 % MgO, has been experimentally confirmed. It has been shown that at basicity of 5 and 4 % of Ce$_2$O$_3$ in slag up to 16 ppm cerium passes into metal during 10 minutes exposure.

1. Introduction

Due to the increase in construction of long gas main pipelines in Russia the research and development of composition of high-strength pipe steels and innovative technological solutions for their production are becoming more and more important for the domestic metallurgy. The promising way of solving the problem is steel microalloying with boron [1–6]. Microalloying of low-carbon boron steel is used to increase the set of mechanical, technological and operational properties while maintaining economically alloyed chemical composition. However, the conditions under which pipelines are laid and operated are characterized, as a rule, by cold climate and high seismic activity, therefore along with high strength the pipe steels have high requirements to impact toughness at low temperatures and deformation ability. However, the ductility of low-carbon steels is related to the impact toughness, the increase in which is accompanied by a decrease in both relative elongation and contraction. One of the directions for solving the problem of maintaining of high strength and providing plasticity of low-carbon steel is organization of the process of modification of metal with rare-earth metals (REM). Positive influence of REM on ductility, impact toughness and resistance to cyclic cracking of pipe steel has been repeatedly confirmed by studies [7–11].

It is known that ferroalloys are used to modify steel with REM. It leads to an increase in the cost of steel. One of the directions of the problem solving can be REM reduction from oxide systems. It is known that introduction of Ce$_2$O$_3$ into the refining slag reduces the activity of harmful Al$_2$O$_3$ inclusions in the metal, melting temperature and slag viscosity, as well as increases the desulfurization
degree [12–18]. In addition, the possibility of reduction of cerium from the slags of the studied oxide system and its dissolution in steel in an amount up to 4ppm is noted, thus providing the effect of steel modification. The microstructure of the molten metal is better refined and consists of ferrite and a small amount of perlite [13–16].

Theoretical and experimental studies of the possibility of cerium reduction by aluminium dissolved in metal from the slags of the CaO–SiO₂–Ce₂O₃–15%Al₂O₃–8%MgO system at temperatures of 1550 and 1650 °C are presented.

2. Materials and methods
The thermodynamic modeling of cerium reduction from slags of the CaO–SiO₂–Ce₂O₃ system containing 15% Al₂O₃ and 8% MgO, by aluminum dissolved in metal at temperatures of 1550 and 1650°C was performed using HSC 8.03 Chemistry (Outokumpu) software package based on Gibbs energy minimization and variational principles of thermodynamics using simplex planning grid method [19–22]. The principle of the method of simplex planning grids is to build a planning matrix, where the basicity of slag and CeO₂ content in slag are changed (Table 1) with the following construction, on the basis of thermodynamic calculations, of mathematical model describing dependence of equilibrium CeO₂ content in metal on slag composition, presented as diagrams ‘the chemical composition of slags of the CaO–SiO₂–Ce₂O₃ system containing 15% Al₂O₃ and 8% MgO—equilibrium content of cerium in metal’ at temperatures of 1550°C and 1650°C (Figures 1 and 2). In diagrams blue lines indicate isolines of equilibrium content of cerium. Thin black lines indicate the basicity of slag (B=CaO/SiO₂), the figures indicate their values.

| № | Slag index | Slag composition, mas. % | [Ce], ppm | B=CaO/SiO₂ |
|---|------------|--------------------------|-----------|-------------|
| 1 | Y₁         | 50.7 25.3 1 15 8         | 0.055 0.085 | 2           |
| 2 | Y₂         | 63.3 12.7 1 15 8         | 1.89 2.68  | 5           |
| 3 | Y₃         | 58.3 11.7 7 15 8         | 11.7 16.1  | 5           |
| 4 | Y₄         | 46.7 23.3 7 15 8         | 0.42 0.64  | 2           |
| 5 | Y₁₃        | 59.1 16.9 1 15 8         | 0.72 1.03  | 3.5         |
| 6 | Y₁₃₂       | 56 16 5 15 8             | 3.47 4.94  | 3.5         |
| 7 | Y₁₂        | 60 12 5 15 8             | 8.77 12.2  | 5           |
| 8 | Y₁₂        | 54.9 21.1 1 15 8         | 0.23 0.34  | 2.6         |
| 9 | Y₁₂₁       | 53.2 20.8 3 15 8         | 0.65 0.95  | 2.6         |
| 10 | Y₂₁       | 61.6 12.4 3 15 8         | 5.43 7.61  | 5           |
| 11 | Y₁₃₁      | 57.5 16.5 3 15 8         | 2.09 3.00  | 3.5         |
| 12 | Y₄¹       | 48 24 5 15 8             | 0.29 0.44  | 2           |
| 13 | Y₃₁       | 54.5 15.5 7 15 8         | 4.85 6.87  | 3.5         |
| 14 | Y₄₂       | 49.4 24.6 3 15 8         | 0.17 0.26  | 2           |
| 15 | Y₃₂       | 50.5 19.5 7 15 8         | 1.62 2.36  | 2.6         |
| 16 | Y₁₂₂      | 51.9 20.1 5 15 8         | 1.13 1.66  | 2.6         |

Experimental studies on reduction of cerium from slag were carried out on the high-temperature unit, made on the basis of the Tamman resistance furnace. Slag from the 58%CaO–12%SiO₂–4%Ce₂O₃–15%Al₂O₃–8%MgO system was used as an experimental slag. Steel containing 0.06 % carbon, 0.25% silicon and 0.05% aluminum was used as metal. A 90 g sample of metal and 9 g slag (10 % of the metal weight) was loaded into a corundum crucible and installed in a furnace, heated and melted. The molten metal and slag were heated up to 1650°C and kept in the crucible for 10 min. Four
parallel experiments were carried out with metal hot soak under the slag of the abovementioned composition in the crucible for 10 min.

Figure 1. Diagram of the equilibrium content of cerium in metal hot-soaked under the slag of the CaO–SiO₂–Ce₂O₃ system containing 15% Al₂O₃ and 8% MgO at the temperature of 1550°C.

Figure 2. Diagram of the equilibrium content of cerium in metal hot-soaked under the slag of the CaO–SiO₂–Ce₂O₃ system containing 15% Al₂O₃ and 8% MgO at the temperature of 1650°C.

Results and discussion
Depending on temperature of metal, basicity of slag and the content of cerium oxide at the expense of the chemical reactions presented in Table 2, from 0.055 to 16 ppm cerium passes into metal. Thus hot soak of the metal containing 0.06 % C, 0.25 % Si and 0.055 % Al, under slag basicity of 2.0, containing 1.0 % cerium oxide, up to 0.055 ppm cerium passes into metal at temperature of 1550 °C. Increase of temperature of system to 1650°C is accompanied by insignificant increase in cerium concentration reaching no more than 0.085 ppm. At increase to 7.0 % of cerium oxide concentration in slag with basicity of 2.0 more essential increase of the content of cerium in metal is observed, reaching in a range of temperatures 1550–1650°C 0.4–0.6 ppm, accordingly.

The growth of basicity of slag favourably affects development of process of reduction of cerium. The increase in basicity of slag from 2 to 5 leads to the increase of the equilibrium content of cerium in the metal from 0.1 to 7 ppm at a temperature of 1550°C (Figure 1). Thus, with temperature increase
to 1650°C the equilibrium content of cerium in metal increases and changes in a considered range of basicity of slag on the average from 0.3 up to 10 ppm (Figure 2).

### Table 2. Gibbs energy change for chemical reactions of cerium reduction

| №  | Chemical reactions                                                                 | ΔG, kJ/mol | 1550°C | 1650°C |
|----|------------------------------------------------------------------------------------|------------|--------|--------|
| 1  | 2Ce₂O₃ + 6Al = CeAlO₃ + 2CeAl₂                                                      | –173       | –164   |
| 2  | CeAlO₃ + 2Al + 3CaO = Ca₃Al₂O₆ + 2CeAl₂                                              | –83        | –84    |
| 3  | CeAl₂ + 1.5SiO₂ = Al₂O₃ + Ce + 1.5Si                                               | –93        | –91    |
| 4  | 3CeO₂ + 4Al + 6CaO = 3Ce + 2Ca₃Al₂O₆                                              | –226       | –233   |

According to the data given in the Table 2 aluminum dissolved in metal interacts with cerium oxides Ce₂O₃, CeO₂ and cerium aluminate CeAl₂O₃ by reactions 1, 2 and 4 with the formation of cerium aluminide CeAl₂, tri-calcium aluminate and metallic cerium. Cerium aluminide CeAl₂ interacting with silicon oxide SiO₂ by the reaction 3 provides the formation of aluminum oxide Al₂O₃ in the slag, cerium and silicon in the metal. However low concentrations of free cerium oxides Ce₂O₃, CeO₂ which do not exceed 0.009 and 0.005%, and free calcium oxide CaO, which do not exceed 2.5 %, in slags formed in the region of reduced to 2.0 basicity and containing no more than 1.0% of cerium oxide, do not provide proper development of the reactions given in Table 2 and, as a consequence, do not provide high concentrations of cerium in metal as well (Table 1). Observed insignificant increase in concentration of cerium in metal with increase in temperature of metal and concentration of free cerium oxides Ce₂O₃, CeO₂, reaching 0.05 and 0.007 %, apparently is caused by development of reactions 2 and 4. Increase in basicity of formed slags to 5.0 is accompanied by increase in concentration of free calcium oxide CaO to 24 % and, as consequence, increase in equilibrium concentration of cerium in metal (Table 1) at the expense of development of reactions 2 and 4.

Hot soak of metal containing 0.06% carbon, 0.25% silicon and 0.05% aluminum under slag containing 58% CaO, 12% SiO₂, 15% Al₂O₃, 8% MgO and 4% Ce₂O₃ is accompanied by reduction of cerium, the concentration of which after 10 minutes of hot soak approaches 16 ppm cerium. At the same time, experimental data practically confirm the results of thermodynamic modeling.

### 3. Conclusions

It is found that from 0.055 to 16 ppm cerium content passes in the steel, containing 0.06% carbon, 0.25% silicon and 0.05% aluminum, depending on the metal temperature, basicity of slag and cerium oxide. Thermodynamic modeling together with the method of simplex planning grids allowed to obtain new data on the equilibrium content of cerium in a metal containing 0.06% C, 0.25% Si, 0.05% Al, hot soaked under the slag of the CaO–SiO₂–Ce₂O₃–15%Al₂O₃–8%MgO system in a wide range of chemical compositions at temperatures of 1550°C and 1650°C. The results of thermodynamic modeling have been experimentally confirmed.

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### References

[1] Ghali S N, El-Faramawy H S and Eissa M M 2012 Influence of Boron Additions on Mechanical Properties of Carbon Steel Journal of Minerals and Materials Characterization and Engineering 11 pp 995–9

[2] Murari F D, Vasconcelos da Costa e Silva A L and de Avillez R R 2015 Cold-rolled multiphase boron steels: microstructure and mechanical properties Journal of Materials Research and Technology 4 (2) pp 191–6

[3] Łętkowska B, Dziurka R and Bała P 2015 The analysis of phase transformation of undercooled austenite and selected mechanical properties of low-alloy steel with boron addition Archives
of civil and mechanical engineering 15 pp 308–16

[4] Lyakishev N P, Pliner Yu L and Lappo S I 1986 Borsoderzhashchiestalii splavy [Boroncontaining steels and alloys] (Moscow: Metallurgia) [in Russian]

[5] Babenko A A, Smirnov L A, Upolovnikova A G and Sychev A V 2020 Theoretical Bases and Technology of Steel Exhaustive Metal Desulfurization and Direct Microalloying with Boron Beneath Basic Boron-Containing Slags Metallurgist 63 pp 1259–65

[6] Babenko A A, Zhuchkov V I, Smirnov L A, Upolovnikova A G, Selminsikh N I and Sychev A V 2017 Formirovanie osnovnyh borsoderzhashchixshchих slakov – perspektivnoe napravlenie vnyechnoi desul'furacii i pryamogo mikrolegirovaniya nizkougliderodistoj stali borom [The formation of the basic boron-containing slags is the perspective direction of the ladle desulfurization and direct microalloying of the low carbon steel with the boron] Ferrous metallurgy: Bulletin of Scientific, Technical and Economical Information 9 (1413) 50-4 [in Russian]

[7] Petryna D Yu, Kozak O L, Shulyar B R, Petryna Yu D and Hredil M I 2013 Influence of alloying by rare-earth metals on the mechanical properties of 17G1S pipe steel Materials Science 48 (5) pp 575–81

[8] Makarchenko V D and Kindrachuk M V 2014 Vliyanie ceriya na mehanicheskii korrozionnye svojstva nizkolegirovannykh trubnyh stalej [The effect of cerium on the mechanical and corrosive properties of low-alloy pipe steels] Kompressionnoe I energeticheskoe mashinostroenie 3 24-9 [in Russian]

[9] Torkamani H, Raygan Sh, Garcia-Mateo C, Rassizzadeghani J, Palizdar Y and San-Martin D 2018 Evolution of pearlite microstructure in low-carbon cast microalloyed steel due to the addition of La and Ce Metallurgical and materials transactions A 49 pp 4495–508

[10] Smirnov L A, Rovnushkin V A, Oryshchenko A S, Kalinin G Yu and Milyuts V G 2016 Modification of Steel and Alloys with Rare-Earth Elements Part 1 Metallurgist 59 pp 1053–61

[11] Smirnov L A, Rovnushkin V A, Oryshchenko A S, Kalinin G Yu and Milyuts V G 2016 Modification of Steel and Alloys with Rare-Earth Elements. Part 2 Metallurgist 60 pp 38–46

[12] Xiaohong Y, Hu L, Guoguang C, Chenghuan W and Bin W 2011 Effect of refining slag containing Ce2O3 on steel cleanliness Journal of rare earths 29 (11) pp 1079–83

[13] Long H 2011 Measurements of physical properties of Ce contained refining slags and their effects on steel cleanliness Master thesis of University of Science and Technology Beijing 32 p 169

[14] Guo M X and Suito H 1999 Effect of dissolved cerium on austenite grain growth in an Fe - 0.20 mass % C - 0.02 mass % P alloy ISIJ International 39 (11) p 1169

[15] Wu C, Cheng G and Long H 2014 Effect of Ce2O3 and CaO/Al2O3 on the Phase, Melting Temperature and Viscosity of CaO-Al2O3-10 Mass % SiO2 Based Slags High Temp. Mater. Proc. 33 (1) pp 77–84

[16] Feifei H, Bo L, Da L, Ligang L, Ting D, Xuejun R, Qingxiang Y 2011 Effects of rare earth oxide on hardfacing metal microstructure of medium carbon steel and its refinement mechanism Journal of rare earths 29 (6) pp 609–13

[17] Wang L J, Wang Q, Li J M and Chou K C 2016 Dissolution mechanism of Al2O3 in refining slags containing Ce2O3 J. Min. Metall. Sect. B-Metall. 52 (1) pp 35–40

[18] Anacleto N M, Lee H-G, Hayes P C 1993 Sulphur Partition between CaO-SiO2-Ce2O3 Slags and Carbon-saturated Iron ISIJ International 33 (5) pp 549–55

[19] Kim V A, Nikolaj E I, Akberdin A A and Kulikov I S 1989 Planirovanie eksperimenta pri issledovani fizo-himicheskih svojstv metallurgicheskixh slakov. Metodicheskoe posobie [The design of the experiment in the study of the physicochemical properties of metallurgical slag. Method book] (Alma–Ata: Nauka) [in Russian]

[20] Kim V A, Akberdin A A, Kulikov I S et al. 1980 Ispol'zovanie metoda simpleksnyh reshetok dlya postroeniya diagram tipa sostav – vyazykost' [Using the simplex lattice method for
constructing composition-viscosity diagrams] *Izvestiya. Ferrous Metallurgy* 9 p 167 [in Russian]

[21] Babenko A A, Zhuchkov V I, Sychev A V and Upolovnikova A G 2016 Ispol'zovanie metoda simpleksnykh reshetok dlya postroeniya diagram sostav-vyazkost' shulakov sistemy CaO-SiO2-Al2O3-MgO-B2O3 [Using of simplex lattices method for diagramming composition-viscosity of the slag system CaO-SiO2-Al2O3-MgO-B2O3] *Butlerov Communications* 48 (11) pp 40–4 [in Russian]

[22] Babenko A A, Zhuchkov V I, Leont’ev L I, Upolovnikova A G and Konysheva A A 2017 Ravnovesnoe raspredelenie bora mezhdu metallom sistemy Fe–C–Si–Al i borsoderzhashchim shlakom [Equilibrium distribution of boron between metal of Fe–C–Si–Al system and boron slag] *Izvestiya. Ferrous Metallurgy* 60(9) pp 752-8 [in Russian]