Metallurgy

Increase of the Efficiency of Direct Doping of Steel by Modeling of the Process of Carbothermal Reduction of Oxide Systems Cr$_2$O$_3$-MnO-SiO$_2$

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ABSTRACT. The present study deals with the problem of raising the efficiency of direct doping of steel and intensification of processes of direct carbothermal reduction of doping elements. Solving of the task of concentration ratios of reacting elements and optimization of temperature limits of the reaction is considered as a rational way for the resolution of the problem. Thermodynamic modelling of kinetics of carbothermal reduction of metals is offered as a key to the problem solution. The problem is discussed on the example of thermodynamic computer modelling of kinetics of carbothermal liquid phase reduction reactions of the complex oxide system of chromium, manganese and silica Cr$_2$O$_3$-MnO-SiO$_2$. It has been substantiated as a result of the study that in the case of choosing and maintenance of rational temperatures of the reaction zone at direct doping of steel it is possible to increase by 10-15% the efficiency of reduction of chromium, manganese and silica and their uptake by the melt. It has been established that maximum possible efficiency of direct doping of steel in conditions of distribution at stoichiometric concentration is achieved at the following ratio of oxide components 20-25 wt% of Cr$_2$O$_3$ and 80-75wt% of [2MnO+SiO$_2$] and maintenance of temperature within 1800-1950 K range in the liquid-phase transition layer of slag-metal. © *2013 Bull. Georg. Natl. Acad. Sci.*

***Key words:** direct doping, reduction of oxides, modelling, thermodynamic analysis.*

According to the world statistics, consumption of iron and manganese ore has increased by 60% and that of chromium ores – half as much over the past ten-year period. Based on the trends in the global industry development experts make prognosis that deficiency of chromium metal ore resources will become noticeable already in 2024, and also the threat of depletion of manganese resources will become real.

Accordingly, the issue of reduction of losses of chromium-manganese resources becomes very urgent, that would only be achieved by modifying the structure of their consumption and development of new resource-saving technologies, which may provide a reduction of redistributions during the overall technological cycle. It is necessary to reduce the number of technological operations both in the cycle of crude

ore enrichment and in the production of mass and structural steel. The reduction in a number of technological operations at mass production of steel and alloys at the first instance implies replacement of application of manganese and chrome ferroalloys by the technology of direct doping by chromium-manganese oxide materials [1]. Ores and concentrates, as well as anthropogenic waste and secondary resources of mining industry can be attributed to such materials.

Modern technology of direct doping refers to the complex process of deoxidization, modification and alloying of cast iron, steel and other iron-carbon alloys that is carried out using the materials, commonly applied for the production of corresponding ferroalloys, basically - oxides or carbonates, and materials containing elements with a high affinity to oxygen can be used as reducers of oxide or carbonate compounds of alloying metals. For example, direct doping technology of steel with manganese in essence, mostly implies the use of alloy addition in the form of manganese agglomerate or briquettes and the reducer in the form of aluminum [2-5]. In this case, the process of doping in steel-melting or steel-pouring installation is organized in such a way which ensures synchronization of melting of briquettes, agglomerate or initial reactant pellets and the reduction process itself. This synchronization is achieved by strict technological methods with the use of initial raw materials of the desired fraction. As a result the process of manganese and chromium reduction is limited by the time of components melting and the rate of chemical reaction. The direct doping technology is not accompanied by the formation of irretrievable losses, the degree of manganese and chromium extraction may reach 95%, while the loss at the outrunnig oxidation (burning) of aluminum does not exceed 5%. But still, in mass and structure steel industry for the purpose of maximum possible resource saving that implies minimization or complete exclusion of use of aluminum, the task of application of a cheaper solid carbon as a reducer arises.

Discussion

In [6] it is proved that, together with aluminum also solid carbon could be applied a reducer. The works [7,8] are also dedicated to the issue of application of solid carbon or carbon-containing organic binder.

In contrast to cases with aluminum reducer, where the reactions are of exothermic character and are carried out in conditions of the auto wave synthesis [9], here application of extra heat sources becomes necessary. This can be easily solved at the implementation of the direct doping process in ladle furnaces for out-of-furnace treatment of melts. In modern steel production, the ladle furnace for out-of-furnace finishing, deoxidation and alloying of steel, mounted on railcar has been used for decades, i.e. this necessity does not make any additional technical complications.

In [7] the results of experiments carried out in the laboratory were published. The possibility of joint reduction of Mn and Cr from a mixture of manganese and chromites concentrates by the optimal amount of a carbon reducer, as well as certain equilibrium reduction of Si are confirmed. The analysis of experimental data of reduction processes was supported by the amount of gasified oxygen as CO and CO_2 and the chemical composition of initial reagents. It is mentioned in the work that high technological parameters of extraction and recovery of alloying elements by steel have been achieved. However, the work is completely of planning-experimental character and does not envisage the additional circumstances that occur in real industrial conditions. First of all, it concerns such disturbing factors of the manganese reduction process as the presence of silica. Even in the considered examples [7] the ratio SiO_2/Mn_2O_3 is equal to 1:1. In the case of application of secondary manganese-containing resources of ferroalloy production the ratio SiO_2/Mn_2O_3 would reach the level up to 2:5 and more, which would radically change the course of reducing reactions and significantly reduce the efficiency of the direct doping process. Results of experiments [7] show that, due to the presence of
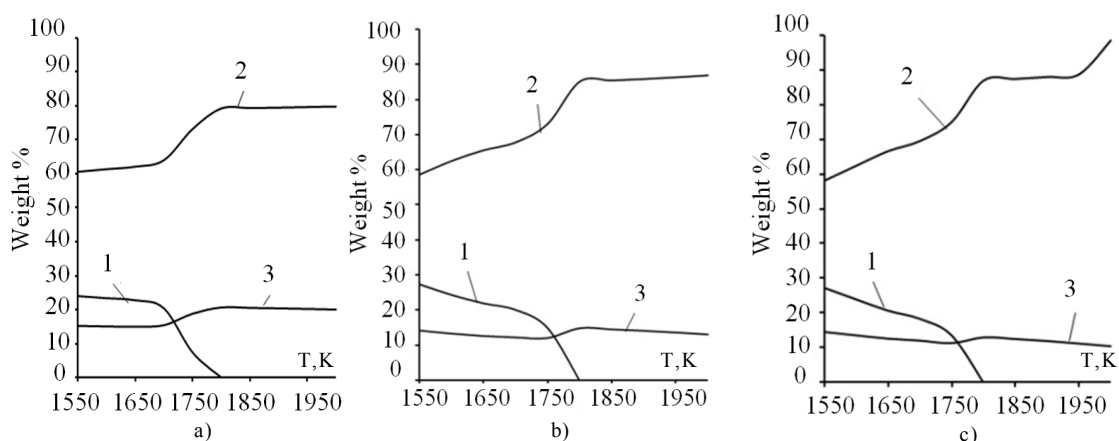
Fig.1. The ratio of condensed phases. 1- Melted slag; 2- Metal solution; 3- Condensed carbon.
    a) at a ratio of components 5-10 wt% Cr_2O_3 and 95-90 wt % ($2MnO+SiO_2$);
    b) at a ratio of components 15-20 wt% Cr_2O_3 and 85-80 wt % ($2MnO+SiO_2$);
    c) at a ratio of components 25 wt% Cr_2O_3 and 75 wt % ($2MnO+SiO_2$);

silica in the manganese concentrate, extraction of useful elements from the mixture of the direct doping reaction on the average makes up to 63% for manganese, up to 82% for chromium and 14% for the silicon itself.

Since silicon is one of the most effective deoxidizer elements of cast iron and steel, its inappropriate use, on the one hand, and worsening of extraction indicators of the deficient chromium and manganese, on the other, prior to the technology of iron-carbon alloys direct doping raise the problem of the necessity of identification of ways for improving the efficiency of the reduction process and maximum possible uptake of target elements.

The solution of this problem first of all requires study of the kinetics of processes of joint carbothermal reduction of chromium, manganese and silicon oxides, and the present work is dedicated to this issue.

As the kinetics of reduction processes is mainly determined by thermodynamic properties of the system of interacting components and reduction process would be carried out in thermodynamic mode, it is possible to model it using thermodynamic equilibrium calculations [10,11]. In contrast to our recent studies [12,13], according to the assigned task, in the present work the factor of the presence of silica SiO_2 is considered, that is a novelty from the viewpoint of thermo-dynamic modelling of carbon-reducing processes in complex oxide systems Cr_2O_3-MnO-SiO_2 for the direct doping technology of alloys.

Material and methods

In the work the multipurpose complexes of ASTRA 4/pc were applied for model thermodynamic calculations. The calculations were carried out in the temperature range 800-2000 K, by 50! step at normal atmospheric pressures.

The following thermodynamic functions of the following elements and compounds were considered while modelling: condensed (C, Mn, Si, Cr, Mn_3C, Mn_7C_3, $Mn_{23}C_6$, SiC, Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$, Mn_5Si_3, Mn_3Si, MnSi, $CrSi_2$, Cr_5Si_3, CrS, Cr_3Si, $CrMn_3$, MnO, MnO_2, Mn_2O_3, Mn_3O_4, SiO_2, Gr_2O_3, CrO_3 $MnSiO_3$, Mn_2SiO_4, $MnCr_2O_4$, Cr_2SiO_9) and gaseous (O, O_2, O_3, C, C_2, C_3, C_4, C_5, CO, CO_2, C_2O, C_3O_2, Cr, Cr_2, CrO, CrO_3, Cr_2O, Cr_2O_2, Cr_2O_3, CrC_2, Si, Si_2, Si_3, SiO, SiO_2, Mn, MnO).

It was assumed at modeling that liquid metal alloy is formed by mutual dissolution of silicides, manganese chromides and carbides obtained after the reduction of these metals and the slag melt is created as the compounds of oxides of silicon, manganese and chromium silicates, and manganese chromites. The main results of model thermodynamic calcula-
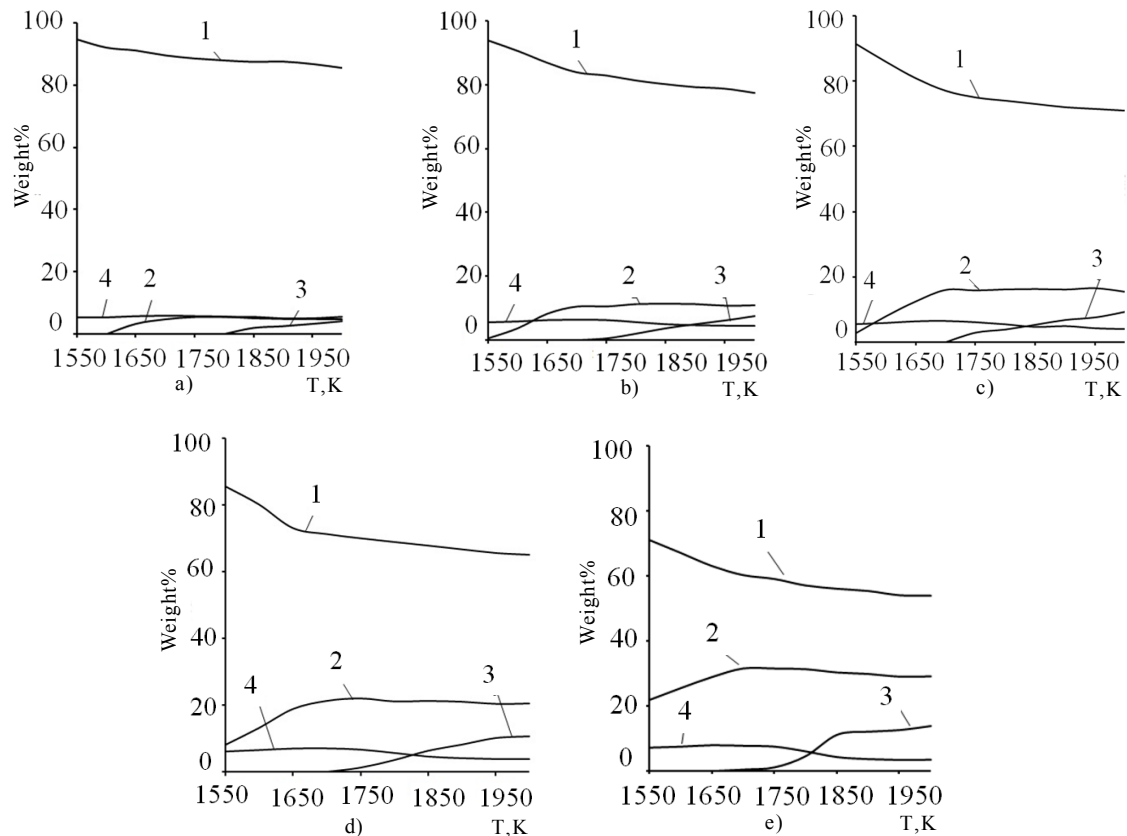
Fig.2. The composition of metal solution
1- Mn; 2- Cr; 3- Si; 4- C, at a ratio of initial components: a) 5 wt% Cr_2O_3 and 95 wt% ($2MnO+SiO_2$); b) 10 wt% Cr_2O_3 and 90 wt% ($2MnO+SiO_2$); c) 15 wt% Cr_2O_3 and 85 wt% ($2MnO+SiO_2$); d) 20 wt% Cr_2O_3 and 80 wt% ($2MnO+SiO_2$); e) 25 wt% Cr_2O_3 and 75 wt% ($2MnO+SiO_2$).

tions are presented in diagrams (Fig. 1, 3), where for each of the compounds the ratios of condensed phases - the slag melt, metal solution and condensed carbon are identified. The composition of the resulting metal solution and the extraction coefficient of the target elements Cr, Mn and Si is also determined, depending on the temperature in the range 1550-2000 K.

It is clear from the diagrams that raising the temperature reduces the slag yield. At temperatures above 1700 K the amount of generated slag intensely decreases. Above 1800 K the slag yield practically ceases and accordingly the amount of metal solution increases. With raising the temperature up to 2000 K metal yield would reach 80-99 wt%. The condensed carbon slightly reduces up to 1700 K, but above this temperature it increases at the expense of separately condensed SiC.

Calculation data on determining the possible composition of the emitted metal solution are shown in Fig. 2. Diagrams show that, depending on the temperature and the ratio of initial oxide components the amount of manganese in the metal solution can be significantly reduced in the range of 1550-1700 K. This can be explained by the accompanying reduction of chromium and silicon. At higher temperatures (1700-2000 K) the content of manganese in the metal solution slightly decreases. The reduced chrome appears in the metal above the temperature 1650 K. In the temperature range 1650-1750 K the amount of reduced chromium significantly increases. Above 2000 K the intensity of release of chromium slightly increases and it may reach 30%. Silicon appears in the metal above 1800 K temperature and its amount increases with increasing the temperature. At 2000 K the amount of silicon metal may reach 10%.
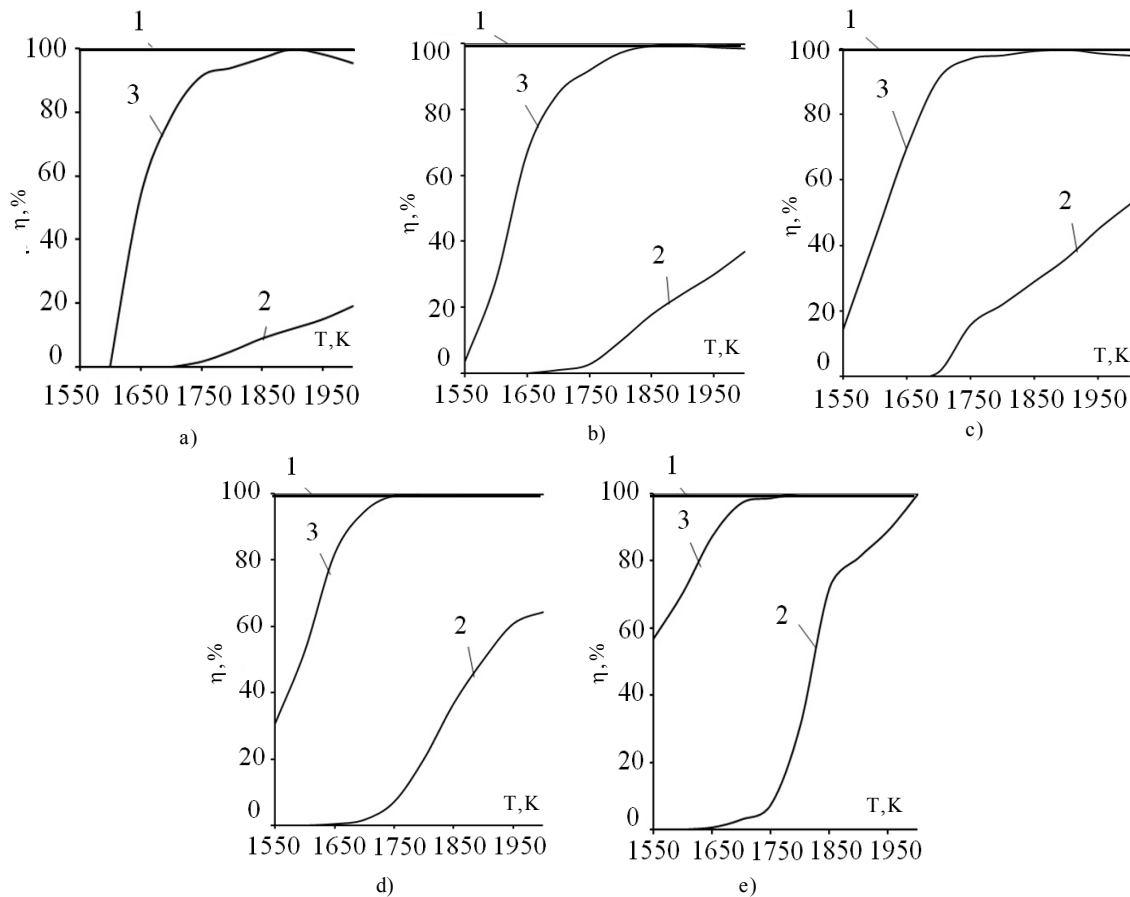
Fig.3. Metal extraction 1- Mn; 2- Si; 3- Cr; at the ratio of initial components:
a) 5 wt% Cr_2O_3 and 95 wt% ($2MnO+SiO_2$); *b)* 10 wt% Cr_2O_3 and 90 wt% ($2MnO+SiO_2$); c) 15 wt% Cr_2O_3 and 85 wt% ($2MnO+SiO_2$); *d)* 20 wt% Cr_2O_3 and 80 wt% ($2MnO+SiO_2$); *e)* 25 wt% Cr_2O_3 and 75 wt% ($2MnO+SiO_2$).

The results of calculation of the metal extraction are presented in Fig. 3. It follows from the diagrams that for the composition (a) of oxide compounds the maximum possible reduction of manganese is already completed at 1550 K temperature. Theoretically the extraction would make up to 99.8 wt%. For silicon, the temperature of possible maximum reduction is equal to 2000 K, the extraction in this case makes up to 19.10 wt%. For chromium the maximum extraction is provided at 1900 K, the extraction would make up to 99.85 wt%. For the composition (b) in contrast to the composition (a) the extraction of silicon increases up to 37 wt%. At the ratio of the components (c) the extraction of silicon makes up to 45 wt%. For the composition (d) the degree of reduction of silicon increases up to 64 % and at the ratio of components (e) the extraction is equal to 99.9%

The analysis of results of modelling the kinetics of the carbothermal reduction of complex oxide systems Cr_2O_3-MnO-SiO_2 shows that the effective implementation of direct doping technology of steel and alloys by chrome-manganese oxide materials requires high temperature in the transition slag-metal layer of the processed metal. In particular, the temperature of the melted processed alloy should not be reduced below 1750 K, and the highest efficiency of direct doping technology is achieved at the ratio of oxide components 20-25 wt% Cr_2O_3 and 80-75 wt% (MnO • SiO_2), while maintaining the temperature of melt within the range of 1800-1950 K.

Consideration in practice of the results of model thermodynamic calculations may essentially improve the technical and economic indices of direct doping technology of iron-carbon alloys. In particular, it

would be possible to provide 99% uptake of manganese and chromium and 84% uptake of silicon.

Conclusion. Thus, it can be concluded that replacement of costly aluminum reducer by cheap solid carbon is advisable in direct doping technology of steel and alloys in conditions of additional external thermal action in the medium of ongoing reduction reactions. Application of modern ladle furnaces may provide stable maintenance of the specified thermal conditions.

Minimization of aluminum consumption and improving of the degree of uptake of chromium, manganese and silicon, despite a slight increase in electric power consumption, will significantly increase the efficiency of the technology of direct doping of iron-carbon alloys.

მეტალურგია

ფოლადის პირდაპირი ლეგირების ეფექტურობის ამაღლება ოქსიდური Gr_2O_3-MnO-SiO_2 სისტემების კარბოთერმული აღდგენითი პროცესების მოდელირებით

ი. ჯანელიძე[*], გ. ჯანდიერი[**], ე. ჯანელიძე[*]

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ნაშრომში განხილულია ფოლადის პირდაპირი ლეგირების ეფექტიანობის ამაღლებისა და მალეგირებელი ელემენტების პირდაპირი კარბოთერმული აღდგენითი პროცესების ინტენსიფიკაციის პრობლემა. პრობლემის გადაჭრის რაციონალურ გზად დასახულია მორგავირე ელემენტების კონცენტრაციული თანაფარდობისა და სარეაქციო ტემპერატურული ზღვრების ოპტიმიზაციის ამოცანის გადაწყვეტა. დასმული ამოცანის გადაწყვეტის გზად შემოთავაზებულია ლითონთა კარბოთერმული აღდგენითი რეაქციების კინეტიკის თერმოდინამიკური მოდელირება. პრობლემა განხილულია ქრომის, მანგანუმისა და კაჟადის კომპლექსური ოქსიდური სისტემის Gr_2O_3-MnO-SiO_2 კომპონენტთა კარბოთერმული თხევადფაზური აღდგენითი რეაქციების კინეტიკის თერმოდინამიკური კომპიუტერული მოდელირების მაგალითზე. კვლევის შედეგად დასაბუთებულია, რომ ფოლადის პირდაპირი ლეგირებისას, სარეაქციო ზონის რაციონალური ტემპერატურული რეჟიმების შერჩევისა და უზრუნველყოფის შემთხვევაში, შესაძლებელია ქრომის, მანგანუმისა და კაჟადის აღდგენისა და თხევადი ნადნობის მიერ ათვისების პროცესის ეფექტიანობის ამაღლება 10-15%-ით. დადგენილია, რომ ფოლადის პირდაპირი ლეგირების მაქსიმალურად შესაძლო ეფექტიანობა აღდგენელი ნახშირბადის სტექიომეტრიული კონცენტრაციით განაწილების პირობებში

მიიღწევა ოქსიდური კომპონენტების კონცენტრაციული განაწილებისას – 20-25 მას.% Cr_2O_3 და 80-75 მას.% [$2MnO+SiO_2$], აღდგენითი რეაქციის მიმდინარეობისას წიდა-ფოლადის თხევადფაზური განშრევების ზონაში ტემპერატურის 1800-1950K ზღვრებში შენარჩუნების პირობებში

REFERENCES

1. *R.S. Takhautdinov, A.I. Nakonechny, V.N. Urtsev, D.M. Khabibulin* (2005), Stal', 5: 20-22. (in Russian).
2. *Yu.N. Nosov, V.P. Komshukov, V.V. Sokolov,* et al. (2004), Stal', 5: 32-35. (in Russian).
3. *M.V. Samsonov* (2006), Author's abstract of Candidate Thesis. Moscow, 20 p. (in Russian).
4. *G. Jandieri, T. Surguladze, D. Robakidze,* et al. (2009), Metal Science and Heat Treatment, **51,**11-12: 553-560, N. Y.
5. *A.I. Nakonechnyi, R.V. Siniakov* (2010), Donbass-2020: Materialy V nauchno-prakticheskoi konferentsii. Donetsk, 973 p.
6. *Yu.P. Vorobiev* (2001), Izvestiia Cheliabinskogo Nauchnogo Tsentra, **4**, 13: 10-14 (in Russian).
7. *S.M. Tleugabulov, E.E. Kiyekbayev* (2008), Priamoe legirovanie stali margantsem i khromom s ispol'zovaniem uglerodosoderzhashchikh kompleksnykh materialov reagentov.
8. *G. Jandieri, D. Sakhvadze, G. Tavadze, T. Surguladze* (2010), Bull. Georg. Natl. Acad. Sci., **5**, 1: 84-88.
9. *A.K. Swiderski* (2009), Izvestiia Tomskogo Politekhnicheskogo Universiteta, **315**, 3: 28-31 (in Russian).
10. *N.A. Dvornikov, S.B. Novichkov* (2004), Tsvetnaia metallurgiia, №8 (in Russian).
11. *N.A. Vatolin, G.K. Moiseev, B.G. Trusov* (1994), Termodinamicheskoe modelirovanie v vysokotemperaturnykh neorganicheskikh sistemakh. Moscow, 352 p. (in Russian).
12. *J. Bagdavadze, G. Gvelesiani, I. Janelidze, K. Ukleba* (2008), Bull. Georg. Natl. Acad. Sci., **2**, 3: 96-98.
13. *Z. Tsikaridze, I. Janelidze, R. Razmadze, J. Bagdavadze* (2011), Bull. Georg. Natl. Acad. Sci., **5**, 3: 76-78.