Journal of Chemical Technology and Metallurgy, 50, 6, 2015, 574-580

ANALYSIS AND OPTIMIZATION OF LADLE TREATMENT TECHNOLOGY OF STEELS PROCESSING

Konstantin Grigorovich[1], Olga Komolova[2], Darina Terebikina[2]

[1] *A.A. Baikov Institute of Metallurgy and Material Science RAS (IMET RAS), 119991 Leninskii prospect 49, Moscow, Russia*
[2] *National University of Science and Technology "MISIS" (MISIS), 119049, Leninskii prospect 6, Moscow, Russia*
E-mail: konstantin.grigorovich@gmail.com

Received 15 February 2015
Accepted 01 September 2015

ABSTRACT

The inclusion control procedures and software for dynamic modelling of ladle treatment technologies were developed to control of steel cleanliness, to detect sources of inclusions origin and to increase the steels quality. The method of quantitative metallography, X-ray microprobe and fractional gas analysis were applied for the basic oxygen species identification and their quantity determination in the probes sampled from the ladle furnace, ladle vacuum degasser and tundish during the ladle treatment and casting of these steels. The ladle treatment technology of 13ХФА steel grade for a pipe lines was optimized. The results of application software through a rational technology of melting and secondary steel treatment were carried out.

Keywords: ladle furnace, thermodynamics, oxide inclusions, steel cleanness.

INTRODUCTION

Modern metallurgical technologies of 21st century provide various methods of ladle treatment to control the quality of steels and alloys. This has led to targeting of very narrow intervals of bulk chemical composition and decreasing of trace in steels. Quality and high level of consumer characteristics of steels is determined by not only their chemical composition and structure but also chemical forms of nitrogen and oxygen, which are present in the matrix, namely, the distribution of the elements between the solid solution and different inclusions, such as nitrides and oxides. Nonmetallic inclusions, which are present in a metal matrix in a significant amount, are known to be main sites of fatigue and tensile crack nucleation, corrosion and damage of steels. Inclusion control and steel cleanliness for the production of tyre cord, bearing, microalloyng high stress steels, steels for railroad wheels and rails is a challenging problem of modern metallurgy. Therefore, to increase the quality of steel, it is important to develop methods for controlling the quantitative and qualitative compositions of inclusions. It is important to choose a proper method for controlling the non-metallic inclusions content in steel and the criteria of estimating the measurement results. The control of non-metallic inclusions allows us to predict the metal properties however modern methods of non-metallic inclusions evaluation are highly labor and time-consuming. Fractional Gas Analysis (FGA) method is a modified oxygen determination method realized under non-isothermal conditions. It is based on the difference in the thermodynamic stability of oxides. It provides a possibility to evaluate and identify oxides in steel. First attempts to elaborate a technique of hot extraction in a carrier gas for the separation of oxides from the steel samples upon monotonous or step-wise heating with IR detector have been tested in [1]. It was found, that the sequence of reduction of different oxides in a carbon saturated melt was predetermined by the standard Gibbs energy of their formation. The progress of earlier works was not, however, succeeded. This fact was mainly attributed to two problems. The first of them was the absence of numerical algorithm and software for data processing of experimental results. The second was a problem of oxide identification. The above problems have been solved on in recent years. First, to process the results of temperature ramped analysis, an OxSeP original software has been developed and implemented on the modern TC-600 LECO gas analyzer [2 - 3]. The numerical procedure involved consecutive separation and subtraction of individual peaks from the total evolution curve. The temperature-dependent background evolutions as well as mixing effects in a gas system of analyzer were also treated by this model. Second, a thermodynamic model of carbon reduction of oxides present in the form of inclusions in a molten sample, saturated with graphite during FGA has improved [4 - 7]. And finally, identification software, which includes a thermodynamic model of carbon reduction of oxide inclusions during the analysis, has been improved [8 - 9]. The oxide reduction processes in carbon saturated iron- and nickel-based melts were investigated [3].

It was shown that combination of quantitative metallography and fractional gas analysis can be used to control the oxide-inclusion cleanness in rail steels. The oxides cleanness of steel estimated from fractional-gas analysis data can be used to predict the service durability of rails [10 - 12].

The modeling of metallurgical processes is a difficult problem which requires the development of physical - chemical models and mathematical algorithms, allowing adequate description of high-temperature processes occurring in open non-equilibrium systems which represent aggregates of ladle treatment of steel. The majority of computer programs, modeling the work of real industrial metallurgical machines, are based on using approximating and statistical models demanding enormous numbers of experimental data. This fact essentially limits possibilities of the modeling programs, which are not capable to sufficiently react to various disturbance and random processes in a wide range of parameters change. One of the main requirements to be submitted to the steel for pipe lines in contact with environment containing hydrogen sulfide, is resistance to stress corrosion cracking and hydrogen embrittlement (HIC). Currently, the production of corrosion-resistant steels for oil and gas pipelines have become a problem of contamination by oxide non-metallic inclusions, which are the cause of the hydrogen stress cracking of steels. Fig. 1 presents the cluster of oxide inclusion found in the focus of hydrogen blister under the surface of steel plate. Typical chemical composition of oxides obtained by EDX spectrometer of Hitachi S-800 scanning electron microscopes is, % mass: Al 31 - 39, Mg 1 - 14, Ca 6 - 14, O 24 - 39.

The aim of this study was to develop mathematical models, algorithms and software for dynamic simulation of ladle treatment technology of steel in ladle treatment and creation of new method of technology optimization using fractional gas analysis method (FGA) and software developed. The next aim of the work was to analyze and optimize the ladle treatment technology of steel 13ХФА production, with the identification of the causes of non-metallic inclusions contamination.

EXPERIMENTAL

Based on the physical and chemical models and thermodynamics the original software for modelling of steel treatment in ladle furnace and vacuum degasser was developed. The target of this software was modeling and on-line control of steel temperature and chemical composition of slag and steel melt during steelmaking processes (ladle-furnace, vacuum degasser). Physical and chemical models based on mass and energy conservation law and principals of non-equilibrium thermodynamics were used. All process stages (zones) were taken into account in this software. It was assumed that the metallurgical systems do not reach equilibrium and are in non equilibrium steady states. In accordance with the L. Onsager, it was proposed that the reaction rate is proportional to the gradient of the chemical potential according to the formulae:

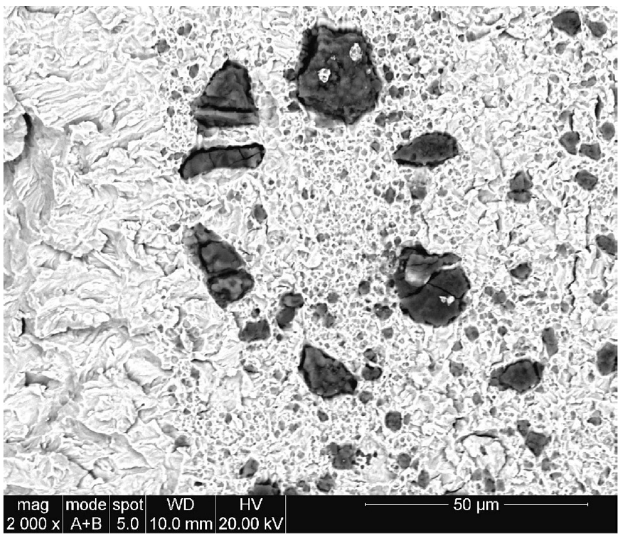

Fig. 1. Oxide inclusions in focus of blister after HIC test. Hitachi S-800 scanning electron microscopes picture.

$$V_i = -SLgrad\mu_i$$

where V_i - reaction speed of i -component, mol/s;

S - interaction surface, m^2;

L - Onsager's coefficient, mol^2/(J·s·m);

$grad\ \mu_i$ - gradient of the chemical potential of i component, J/(mol·m).

All components in the interaction zone in the slag-metal system are equal to the turbulent mass transfer conditions. Therefore it was assumed that the surface area of interaction, Onsager coefficients, temperature and boundary layer thickness - δ are the same for all reactions. If the coefficient β is:

$$\beta^* = SL\frac{1}{\delta}$$

then the reaction speed of i –component is:

$$V_i = \beta^* RT \ln\frac{K_r}{K_e}$$

where K_e and K_r are equilibrium and real reaction constants.

To calculate the reaction rates of interactions between components of slag-metal system was developed by an iterative algorithm. Model defines a direction of chemical reactions for metal-slag system which are presented as a matrix of k reactions and takes into consideration mass and energy balance equations.

This software takes into consideration input data such as: temperature, slag and metal mass and compositions, input time and mass of additives, blowing, electrical and time regimes.

Additional data which is to be used in calculations are ladle equipment facilities (ladle geometry, transformer parameters, electrode consumption, number of lances, type of refractory materials), thermodynamic database, thermal, physical and chemical databases for additives and inert gas, production database (for statistics). It was demonstrated that the software is stable even after changes in technological scheme.

Mathematical model consists of the following blocks:

- Calculation the speed of interaction between the components in the slag-metal system;
- Calculating the amount of metal and slag in the interaction zone depending on the power of stirring of the bath;
- Calculation of the mass of metal and slag;
- Calculation of the chemical composition and temperature of the slag and metal bath.

Validation of mathematical model and a checking the adequacy of the software was performed on the ladle treatment data industrial heats of steels for pipe lines of metallurgical steel plant.

The oxygen content in the samples and cleanness control evaluation was determined using the TC-600 LECO analyzer and the original OxSeP software.

Fig. 2 shows results of typical FGA data processing

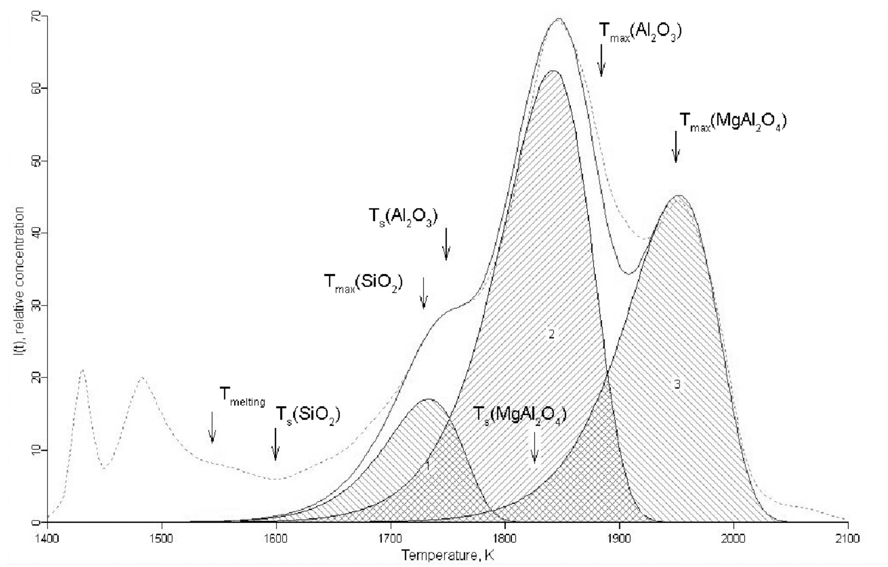

Fig. 2. FGA result for a steel sample. The arrows indicate calculated parameters: T_s - the start temperature of the oxide reduction; T_{max} - the temperature of peak maximum.

for a steel sample. The curve of CO evolution from the specimen is a sum of peaks. Each peak results from the reduction of a particular kind of oxide inclusions.

With the increasing of temperature, the oxide particles RxOy present in the melt are reduced with carbon with the formation of CO bubbles nucleated on the particle surfaces. The reduction of the oxide in the carbon-saturated melt with the oxide-forming component, passing into the solution, develops according to the following reaction:

$$\boldsymbol{R}_x\boldsymbol{O}_y\,(s) + y\boldsymbol{C}(gr) = x\boldsymbol{R} + y\boldsymbol{CO}(g),$$

where the equilibrium constant of reaction is:

$$K_p = \frac{a_R^X \cdot p_{CO}^Y}{a_C^Y \cdot a_{RxOy}}$$

where R - the oxide forming element; x, y - the stoichiometric coefficients, K_p - the reaction equilibrium constant characterizing the stability of oxides; a_C, a_{RxOy}, a_R - carbon, oxide and deoxidizer activities, respectively, and p_{CO} - the partial pressure of carbon monoxide.

Basing on the equilibrium constant for considered reaction it is feasible to evaluate actual temperatures of carbon oxide reduction beginning in melt. In the absence of oxide-metal mutual solubility, basing on Gibbs energy equation, we can directly estimate the temperature, at which the carbon monoxide pressure reaches a desired value:

$$\Delta G \equiv y(\Delta G^0_{CO} + RT\,\ln p_{CO}) + RTx\,\ln(x_R\gamma_R) - \Delta G_{RxOy} = 0,$$

where x_R, γ_R are mole portion and Raul activity coefficient of deoxidizer in melt; ΔG^0_{CO} is the change of standard Gibbs free energy of CO formation, J/mole; ΔG_{RxOy} is the standard free energy of oxide formation from pure liquid metal and gaseous oxygen, J/mole.

The activity coefficient of deoxidizer in the carbon-saturated melt carbon can be expressed in terms of interaction parameters. The next fundamental principles of oxide identification in the FGA method can be specified as follows: for a given melt composition, each oxide has own temperature range of carbon reduction. Based on the equilibrium constant for considered reaction, it is feasible to evaluate the actual temperatures of oxide reduction starting in the melt. The software developed calculates identification parameters - the temperature of the oxide reduction start Ts, the temperature of peak maximum Tmax, to define certain kind of supposed oxide inclusions in the steel grade. As a final result of the real experimental data treatment by “OxSeP”, one can obtain the total oxygen and surface oxygen contents, oxygen content in oxides as a sum of oxygen corresponding to peaks and a set of oxygen content for each peak having its own model temperatures. Using the FGA data, we can rapidly determine the volume fraction of oxide inclusions in the steels.

Using the FGA data, we can rapidly determine the volume fraction of oxide inclusions in steels. This parameter, characterizing the cleanness of steel, is estimated by quantitative metallography, and is controlled by a number of documents such as DIN 50602, method K; ASTM-E45, method D. Since FGA can quantitatively determine the oxygen content in each type of inclusions, we can easily show that the volume fractions of oxide inclusions V_{oxides} can be calculated to a higher accuracy as compared to that providing by metallographic methods using formula:

$$V_{oxides} = \frac{\rho_{steel}}{100}\sum_{i=1}^{n}\frac{O_{OX}M_{OX}}{\rho_{OX}\,yM_O}$$

where ρ_{steel} and ρ_{OX} are the density of steel and oxides of a given composition, respectively; M_O is the atomic mass of oxygen; M_{OX} is the oxide molecular mass; y is the stoichiometric coefficient outside oxygen atom in oxide and *Oox* is the FGA determined content of oxygen (mass %) fixed in the oxide of this type of inclusions [11 - 12].

RESULTS AND DISCUSSION

The probes of steels were sampled (dual samples) from the ladle furnace, RH degasser and tundish during all steps the ladle treatment technology. Chemical composition of steel for a pipe line is presented in Table 1. The steel samples were taken at the main processing stages, listed in Table 2. The methods of quantitative metallography, X ray microprobe and fractional gas analysis (FGA) were applied for the non-metallic inclusion characterisation and quantification. The chemical compositions of the steels were determined on GDS-850 LECO glow-discharge atomic emission spectrometer. Metallographic examination was performed on an Olympus PME-3 optical microscope and Hitachi S-800 scanning electron microscopes. The total oxygen in these steel

Table 1. Chemical composition of steel for a pipe line, % mass.

C	Si	Mn	S	P	Cu	Ni	Cr	V	Al	N
0,05-0,07	0,25-0,35	0,55-0,70	0,002	0,012	0,25	0,30	0,360-0,70	0,07-0,09	0,02-0,05	0,008

samples and oxygen content in different oxide inclusions was determined using the TC-600 LECO analyzer and the original OxSeP software. The FGA results were compared with data obtained by Image analysis on IA-32 LECO Analyzer and X-ray microprobe analysis. The obtained results showed the high reproducibility of the oxide characterisation procedure. The volume fraction of inclusions obtained by FGA method clearly illustrates the contamination of steel.

Fig. 3 presents the FGA results: the mean values and standard deviation for probes that were sampled from the ladle furnace (LF) and the ladle vacuum degasser (RH) during the ladle and vacuum treatment of steel. All the peaks were divided into three groups according to the chemical composition of oxides identified using by the original OxSeP software. The first group of peaks with Tmax < 1750 - 1770 K was attributed to silica and manganese silicates.

The second group of peaks was attributed according to the calculations to alumina and complex spinels which are more harmful for these steels. The third group of peaks was attributed to complex (Mg and Ca-rich) - silicates.

Fig. 3 allows us to estimate the influence of all steps of ladle treatment on the total oxygen and nitrogen contents as well as the amount and content of different oxide inclusions in the steel melt.

The total oxygen content and oxygen in the form of silicates, alumina and alumina silicates of calcium (alumina-magnesium spinel) correspond to the volume fractions of respective types of inclusions in the melt. Left scale of ordinates represents the concentration of oxygen in the three types of oxides (silicates, aluminates and alumina silicates of calcium) and the amount of aluminium dissolved in the melt and associated with oxygen.

Right scale of ordinates indicates the total nitrogen and oxygen in the steel melt.

It is shown that the FGA application allowed us to find a number of harmful oxide inclusions - aluminium silicates and spinels, identified as non-deformable, to predict their influence on the steel quality and to detect sources of their origin during the ladle treatment process. The procedures of cleanliness control for tire cord and railway steels by the Image analysis and FGA were developed.

For testing of software and validation of the model, the results of ladle treatment of 25 real heats of steel for pipe line and sampling control results were used. On Fig. 4 are presented comparative results of calculated values obtained by the software and results of chemical composition control of the metal melt during the treatment

Table 2. Sampling of steel in the course of full-scale experiments.

Sample	Place and time of sampling
EAF	After the tapping melt in ladle from the electric arc furnace
LF-1, LF-2, LF-3	Upon treatment in the ladle furnace: 1 - after installation; 2 after the first, second heating; 3 after the last treatment.
RH-1	After vacuum treatment
RH-2	10 minutes after degassing and refining with argon
RH-3	10 minutes after degassing and refining with argon
MS	From tundish, in the middle of casting

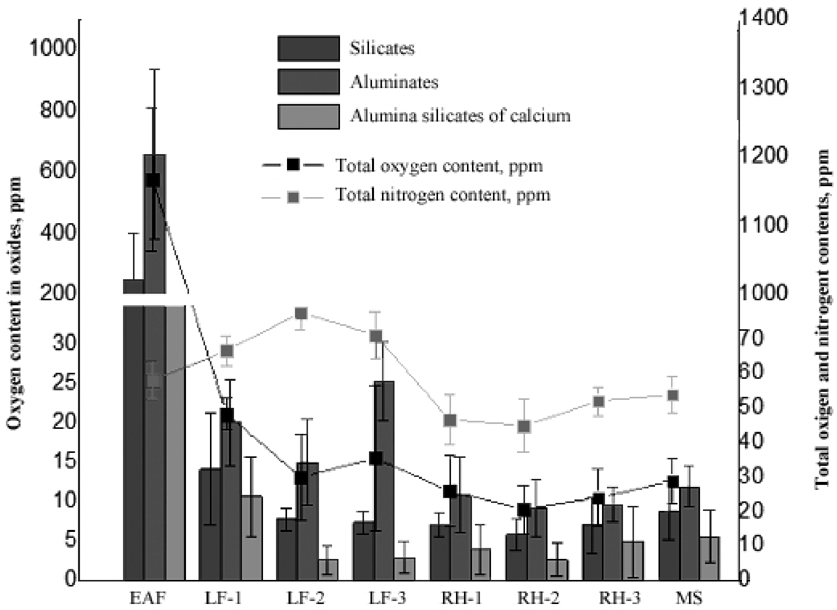

Fig. 3. The total oxygen and nitrogen contents and content of different oxide inclusions in the steel melt.

at the ladle furnace. It is shown that software designed allows us to make dynamic simulation and optimization of ladle treatment technology. It was established that the software to adequately describe the dynamic changes of the basic characteristics of the metal, slag and reaction of system on the process control feedback. The resulting standard deviations of the calculated and experimental values (Fig. 3) is: [Mn] - 0.11; [C] - 0.015; [Si] - 0.02;

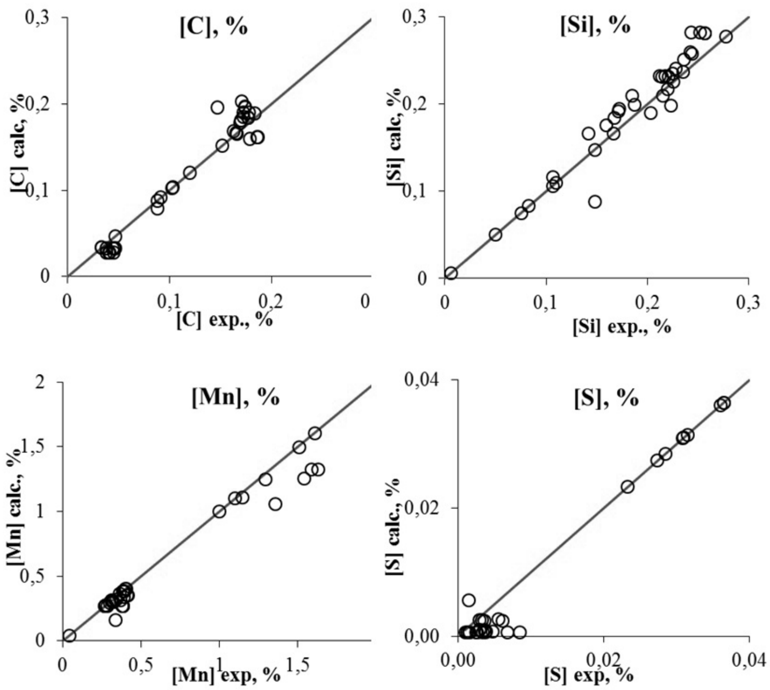

Fig. 4. Comparison of calculated values obtained by the software and chemical composition results of chemical composition control of the samples of molten metal during processing at the ladle furnace.

[P] - 0.0005; [S] - 0.0026; temperature - 17°C. It has been shown that the use of the software developed for the dynamic simulation of ladle treatment of steel and fractional gas analysis method allows to optimize the secondary treatment technology. This software can be used in online calculations and control of process parameters during ladle treatment, modeling and optimization of ladle treatment technology, teaching and training of steelmaking staff.

CONCLUSIONS

Fractional gas analysis method to provide the favourable composition of oxide inclusions and software for dynamic simulation of ladle treatment technology to increase the steels quality were used. The ladle treatment technology of steel for pipe lines was optimized using combination of dynamic simulation of ladle treatment processes was designed. It was shown that software designed allows us to proceed the dynamic simulation of ladle treatment technology, to optimize one and to lead the process within an optimal way. It was shown that the FGA application allowed us to find a quantity of harmful oxide inclusions - aluminum silicates and spinels, identified as non-deformable and to detect sources of their origin during the ladle treatment process. The procedures of steel cleanliness control for steels by using the FGA were developed. It results in reduction of energy, additives and costs and steel quality increasing.

Acknowledgements

The work is financially supported by Federal task program "Research and development on priority directions of development of scientific and technological complex of Russia on 2014-2020" № 14.578.21.0023 of Ministry of Education and Science of Russia. Project unique identifier RFMEFI57814X0023.

REFERENCES

1. R. Prumbaum, K. Orths, Verfahren und die Schnellbestimmung von Gaseninsbesondere des Sauerstoffes und derv or-liegenden Bindungsformen in Metallen, Gießerei Forschung, Bd 31, 2/3, 1979, 71-82.
2. K.V. Grigorovitch, A.M. Katsnelson, A.S. Krylov, A.V. Vvedenskii, New approach to the fractional gas analysis application in metallurgy and material control using oxide separation software developed, Proceedings of 4th Int. Conf., Analytical Chemistry in the Steel and Metal Industries (CETAC), Luxembourg, 1995, 527-532.
3. K.V. Grigorovitch, P.V. Krasovskii, A.S. Krylov, Fractional Gas Analysis - Basic Principles and Application in Steel Quality, Proceedings of the 50th Chemists Conference, British Steel, U.K. British Steel plc. Teesside Technology Centre 1999, 129-131.
4. K.V. Grigorovitch, P.V. Krasovskii, S.A. Isakov, A.A. Gorokhov, A.S. Krylov, Processing and interpretation of fractional gas analysis results: Industrial Lab., Diagnostic of Materials, 68, 2002, 9, 3-9.
5. K.V. Grigorovitch, P.V. Krasovskii, Fractional gas analysis of Al_2O_3 и SiO_2 inclusions in iron base alloys by currier gas hot extraction method: Industrial Lab., Diagnostic of Materials, 68, 2002, 10, 17-24.
6 P.V. Krasovskii, K.V. Grigorovitch, Thermodynamics of nonisothermal reduction of oxide inclusions in carbon saturated melts, Russian Metallurgy (Metally), 2, 2002, 108-113.
7. K.V. Grigorovich, Nonisothermal reduction of oxides in carbon-saturated melts, Journal of Physics: Conference Series, 98, 2008, 3, 032012.
8. K.V. Grigorovich, New possibilities of modern methods for determining gas-forming impurities in metals, Inorganic Materials, 44, 2008, 14, 56-69.
9. S.S. Shibaev, K.V. Grigorovitch, Deoxidation with silicon and the control of oxide inclusions in electrical steels: Russian Metallurgy (Metally), 2, 2006, 108-118.
10. K.V. Grigorovich, A.K. Garber, S.S. Shibaev et al., Increasing the Quality and Operating Conditions of Rails and Rail Joints (Materials of Rail Commission 2008), 2009, 150-168.
11. K.V. Grigorovitch, K.Yu. Dyomin, A.M. Arsenkin, A.K. Garber, Application of Ba-bearing master alloys for deoxidation and modification of railroad steels, Metally, 5, 2011, 146-157.
12. P.V. Krasovskii, W. Gruner, K.V. Grigorovitch, Improving the procedure for oxide speciation in steel by inert gas fusion technique, Steel Research, 77, 2006, 1, 50-58.