

UDC 669.187.26

DOI: 10.17580/cisr.2018.02.03

IRON OXIDATION STATE ANALYSIS IN OXIDE-FLUORIDE SLAGS

L. Ya. Levkov¹, D. A. Pankratov²¹ JSC «RPA «CNIITMASH» (Moscow, Russia)² Lomonosov Moscow State University (Moscow, Russia)

E-mail: LYaLevkov@cniitmash.com, 6758745@mail.ru, pankratov@radio.chem.msu.ru

AUTHOR'S INFO

L. Ya. Levkov, Dr. Eng., Head
of the Special Electrometallurgy
Laboratory,
D. A. Pankratov, Cand. Chem.,
Leading Scientific Researcher,
Chemical Dept.

Key words:

iron oxidation state, oxygen partial
pressure, electromotive force (EMF),
Mössbauer spectroscopy, beads.

ABSTRACT

Development of significant provisions of the slag melts theory made it possible to substantiate a change in the average oxidation state (o.s.) of iron in the slag phase, and also to determine the conditions and limits of such changes. It is shown that the value of the equilibrium oxygen partial pressure, P_{O_2} as a value available for measurements is possible to be taken as a measure of slag redox potential of, taking into account its electronic system performance (the Fermi level). It is established a functional relationship between the average o.s. of iron in the oxide-fluoride melted slags, P_{O_2} value and the temperature. Taking into account the structural peculiarities of the external iron electron shells, a kind of dependence of its average o.s. in the slag phase on P_{O_2} was proposed and it was experimentally established that a decrease in P_{O_2} from 10^{-6} to 10^{-10} Pa at 1873 K leads to a decrease in by o.s. approximately a factor of 2. An increase in the iron content in a slag leads to a monotonous increase in its average o.s. The study of Mössbauer absorption spectra of quenched slag samples confirmed the possibility of simultaneous presence of iron in the slag in oxidation states from 0 to +3.

Introduction

Electronic structure of transition elements — $(n - 1)d^xns^y$ determines the number of possible oxidation states (o.s.) of each element, which corresponds to its unique nature. This is one of the fundamental properties, which depends on the distribution of the electron density and the bond character that are represented by physical research methods reflecting the fluctuations of electronic states.

A feature of a melted slag, containing the transition elements (iron, chromium, manganese, titanium) is the variation of its redox properties within a wide range as a result of the change in the o.s. of these elements [1, 2]. Despite the fact that in many cases the deviation areas of slag compositions in comparison to stoichiometrical are very small, these deviations affect significantly not only their redox properties, but also sorption, electrical, diffusion and other characteristics. Theoretical and experimental studies of slag melts with a large variety of the manifested o.s. of d-elements are of considerable interest.

Fundamental part

However, the state of the slag phase cannot be fully described by indicating only the temperature, pressure and nominal chemical composition. Additional data are required documenting the level of redox potential. The proposition to take into account the characteristics of the electronic phase system [3, 4] lead to an expression for the component chemical potential:

$$\mu_{(i)} = \mu_{(i)}^0 + RT \ln a'_{(i)} + \mu v_i, \quad (1)$$

where $\mu_{(i)}$ — chemical potential of i component in slag; $a'_{(i)}$ — i element activity fraction, which is only dependent

on the nominal (analytical) composition of the phase; μ — chemical potential of the electrons in a phase (the Fermi level); v_i — average i element o.s. in slag phase; R — absolute gas constant; T — absolute temperature.

Average o.s. of k elements, that are an integral part of the phase, related to the electroneutrality equation:

$$\sum_{i=1}^k n_{(i)} v_i = 0, \quad (2)$$

where $n_{(i)}$ — the number of moles of i element in slag phase. Value v_i is the difference between the number of electrons in an atom of i element (its number in the periodic table) and the average number of electrons at the energy levels of the atoms of this element in the phase. It is determined by equation [3, 4]:

$$v_i = v_i^{\max} - S_i + \sum_{j=1}^{S_i} f(E_{ij}) = v_i^{\max} - S_i + \sum_{j=1}^{S_i} \left[1 + \exp\left(\frac{\mu - E_{ij}}{RT}\right) \right]^{-1}, \quad (3)$$

where v_i^{\max} — integer value of the o.s. of i element; S_i — a number of energy levels with variable occupation; E_{ij} — energy levels of j atoms of i element.

The theoretical analysis shows that for slags having a composition with a narrow nonstoichiometry interval, which are characterized by a weak dependence of v_i on μ , a small change in the composition of the phase must be accompanied by a significant change in its redox potential.

If the slag is in thermodynamic equilibrium with the gas phase at partial oxygen pressure P_{O_2} , then the chemical potentials of oxygen in gas $\mu_{(O)}$ and slag $\mu_{(O)}$ are equal. To assess changes in o.s. of elements that make up the slag phase, oxygen is used as reference element: $v_O = -2$. This step allows taking the value of the equilibrium partial pressure of oxygen as a measure available for measurements in the quality of the redox potential of the slag.

$$\begin{aligned}\mu_{\{0\}} &= \mu_{\{0\}}^0 + \frac{1}{2}RT \ln P_{O_2} = \\ &= \mu_0 = \mu_{(0)}^0 + RT \ln a'_{(0)} - 2\mu\end{aligned}\quad (4)$$

Further analysis makes it possible to express the features of the structure of the outer iron electron shells $3d^64s^2$ ($i = Fe$) by the dependence of its average o.s. in the slag phase on the energy states of the element and the Fermi level:

$$\begin{aligned}v_{Fe} &= \left[1 + \exp\left(\frac{\mu - E_{Fe4s^1}}{RT}\right)\right]^{-1} + \\ &+ \left[1 + \exp\left(\frac{\mu - E_{Fe4s^2}}{RT}\right)\right]^{-1} \\ &+ \left[1 + \exp\left(\frac{\mu - E_{Fe3d^6}}{RT}\right)\right]^{-1}\end{aligned}\quad (5)$$

Assuming that $\mu_{(0)}^0 = \text{const}$ and accepting assumption about zero width of 4s iron zone, we have:

$$\begin{aligned}E_{Fe4s^1} = E_{Fe4s^2} &= \mu_{(0)}^0 - \frac{1}{4}RT \ln P_{O_2}^{Fe1}; \\ E_{Fe3d^6} &= \mu_{(0)}^0 - \frac{1}{4}RT \ln P_{O_2}^{Fe2},\end{aligned}\quad (6)$$

where $P_{O_2}^{Fe1}$ and $P_{O_2}^{Fe2}$ — constants at a given temperature, which values can be calculated on the basis of data [5] on the dependence of liquid iron oxides composition on P_{O_2} . Relation (5) and relation (6) following the transformations and simplifications, imply a functional relationship between o.s. of iron in the slag melt and P_{O_2} value, which is available for experimental control [6]:

$$v_{Fe} = 2 \left[1 + \left(\frac{P_{O_2}^{Fe1}}{P_{O_2}}\right)^{1/4}\right]^{-1} + \left[1 + \left(\frac{P_{O_2}^{Fe2}}{P_{O_2}}\right)^{1/4}\right]^{-1}\quad (7)$$

Of course, the assumption of “zero width” of a number of energy levels of the transition elements is not strict. But it allows for interpreting the experimental data and obtaining practically useful recommendations.

Experimental study of o.s. components of slag melt showing the effect of slag oxidation (P_{O_2}) on its chemical and phase composition, the electronic conductivity [7, 8] — difficult task, due to small changes in the chemical composition of the latter. The EMF method has a high sensitivity even with respect to minor changes in slag composition. The results of measuring P_{O_2} and iron o.s. checking in oxide-fluoride slags are described in publications [9, 10].

The Mössbauer spectroscopy method can be considered a reliable method for determining the charge state of iron atoms in metallurgical slags [11]. Thus, the value of one of

the main parameters of Mössbauer spectra description — the isomeric shift — is determined by the value of electron density of 1s-electrons on the iron atom nucleus, which is primarily related to the electronic configuration of the outer (valence) atom levels. As for oxygen and fluoride iron compounds, a dependence of values of the isomeric shift on the formal iron o.s. is observed in compounds close to linear [12, 13]. The relative areas of the Mössbauer spectra resonance lines are proportional to the relative content of the iron-containing phase component they correspond to. Thus, the Mössbauer spectroscopy method is a direct method that allows differentiating iron compounds in complex composition materials according to o.s. The main problem in the study of low-iron materials by Mössbauer spectroscopy is the small content of ^{57}Fe isotope in natural iron. However, the use of the initial iron compounds enriched by ^{57}Fe isotope makes it possible to obtain Mössbauer spectroscopy data for complicated study objects.

Experimental part

For experiments on a laboratory resistance furnace with the graphite heater slags (**Table 1**) were preliminary calcined in air at 1073 K for 2 hours by fusing them in crucibles of boron nitride. In addition, C2 slag was studied, which is used for ladle steel refining, as well as fluxes of electroslag remelting — ANF-1 and ANF-6.

The melts were added with successively increasing Fe_2O_3 powder addition from 0.05 to 3.0% of their original weight (0.1 kg). At the same time, a short-term slag foaming was recorded, upon which P_{O_2} measurement and sampling were performed.

The first small portions of Fe_2O_3 led to a significant decrease in EMF (an increase in P_{O_2} by 1.5–3 orders). The effect of subsequent additives turned out to be weaker. Such results are distinctive in all study slags.

With the introduction of large Fe_2O_3 additives (0.5–3.0% of the initial mass of the melt), metal beads were isolated from the slag. Beads collected from the bottom of the crucible were subjected to chemical analysis. The content of oxygen and carbon was within 0.0015...0.0030% and 1.6...3.1% respectively. To determine these contents the high-temperature extraction method after preliminary electropolishing of the beads surface was used. The content of aluminium was within 0.02...0.20%. To determine this content the spectral analysis method in the inductively-coupled plasma was used. Absolute permissible discrepancies intra-assay are characterized by the following values, %: [C] ± 0.02 , [Al] ± 0.005 , [O] ± 0.0004 .

Slag samples were taken by freezing on a tungsten core, placed in liquid nitrogen and then analyzed by X-ray fluorescent method. The error in determining Fe concentration in the slag was 0.02%.

The relation of P_{O_2} with iron concentration in the slag expressed in its atomic fraction C_{Fe} , shown in **Fig. 1**. The line 4 in **Fig. 1** is drawn on the assumption of stoichiometric composition of iron oxide (II) and represents

Table 1. Initial chemical composition of the study slags

Slag type	Component content/ % wt.							
	CaF ₂	MgO	Al ₂ O ₃	SiO ₂	CaO	FeO	MnO	Other, Σ
C1	–	–	40.0	–	60.0	–	–	–
C2	11.0	23.2	22.4	13.1	30.0	0.10	0.1	0.10
ANF-6	62.6	0.7	29.6	2.6	4.2	0.11	0.1	0.09
ANF-1	85.8	1.0	3.5	3.2	6.2	0.11	0.1	0.09

the dependence of the iron content in the slag on P_{O_2} in this hypothetical case. The experimental curves obtained for the studied slags are non-linear. The tangent of the angle between the line tangents to them and the axis of abscissas increases progressively as P_{O_2} increases. This fact makes it possible to assess the value of v_{Fe} and its changes when P_{O_2} changes using the relations proposed in the paper.

The experimental points in Fig. 2 represent the results of the above described laboratory studies, as well as literature on other slags [14–20]. The curves were calculated based on relation (7) taking into account data [5] in the temperature range of 1523–2023 K.

In order to confirm the relationship of the average iron o.s. in slags with P_{O_2} , the Mössbauer spectroscopy method was used to differentiate iron atoms with different o.s. In doing so, the samples of slag with the iron oxide (III) addition of natural isotopic composition in the range from 0.05 to 3.0% were studied as well as specially prepared samples using $^{57}Fe_2O_3$ as an iron source with an enrichment level of 95% (iron content in slag from 0.5 to 2.0%). The samples were quenched in liquid nitrogen on tungsten or graphite rods.

Mössbauer absorption spectra of slag samples were obtained on MS104EM express spectrometer produced by “Cordon”. ^{57}Co in the matrix of metallic rhodium with an activity of 1 and 25 mCi produced by “RITVERC” served as the source of γ -radiation. The presence of resonant lines was monitored both in wide and narrow velocity ranges. Because of the low iron content in the samples to achieve an acceptable quality of the spectra, the spectral data was collected for a long time (up to 2 months). As a result, the temperature of some samples varied within the range of +17...+28 °C. Mathematical processing of the experimental Mössbauer spectra was carried out at high resolution (1024 points) using SpectrRelax 2.4 and Univem MS 9.08. For this purpose, the spectra were

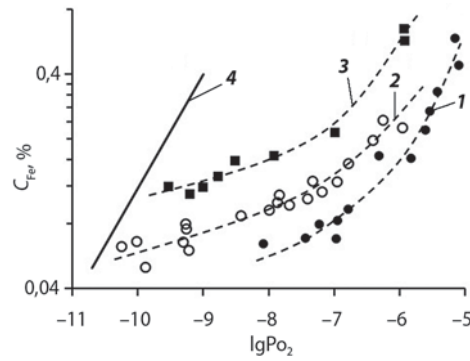


Fig. 1. The relationship of lgP_{O_2} with iron concentration in oxide-fluoride slags at 1873 K [6]: 1 – ANF-1; 2 – ANF-6; 3 – C2; 4 – is drawn on the assumption of stoichiometric composition of iron oxide (II)

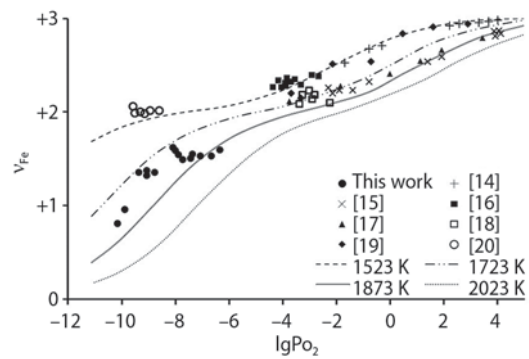


Fig. 2. Dependence of the average iron o.s. in slags on lgP_{O_2}

described by superposition of singlets, symmetrical doublets and sextets. The weakly pronounced effects observed for the study samples required taking into account the effect of iron admixture in the material of the beryllium window of the spectrometer detector on the spectra. In this regard, spectrum parameters without a sample-absorber (background level) were previously

Table 2. Parameters of Mössbauer spectra of ANF-6 slag samples

Sample reference code	Sampling time interval /s	Additive mass fraction Fe / %	δ /mm/s	Δ /mm/s	Γ_{exp} /mm/s	H_{eff}/T	S(k)/ %	$v_{Fe}(k)$	Average v_{Fe}	
Background			1	0.13	0.57	0.26	100			
2-1	5	0.5	1	0.00	0.00	0.30	33.0	41	0	+1.18
			2	0.96	0.44	0.31		22	+2	
			3	0.76	1.43	0.55		27	+2	
			4	1.35	1.47	0.30		10	+2	
2-2	5	1.5	1	0.00	0.02	0.22	32.9	8	0	+1.84
			2	0.94	0.57	0.32		25	+2	
			3	0.81	1.38	0.61		45	+2	
			4	1.26	1.52	0.64		22	+2	
2-3	5	2.0	1	0.90	0.83	0.55		30	+2	+2.04
			2	0.94	1.72	0.91		66	+2	
			3	0.34	0.73	0.25		4	+3	
1-1- ^{57}Fe	5	0.5	1	0.00		0.20		4	0	+1.80
			2	0.23	-0.07	0.74	18.2	36	0	
			3	0.29	0.55	1.19		60	+3	
1-2- ^{57}Fe	900	0.5	1	-0.08	0.00	1.00	27.6	68	0	+0.96
			2	0.25	0.68	0.83		32	+3	

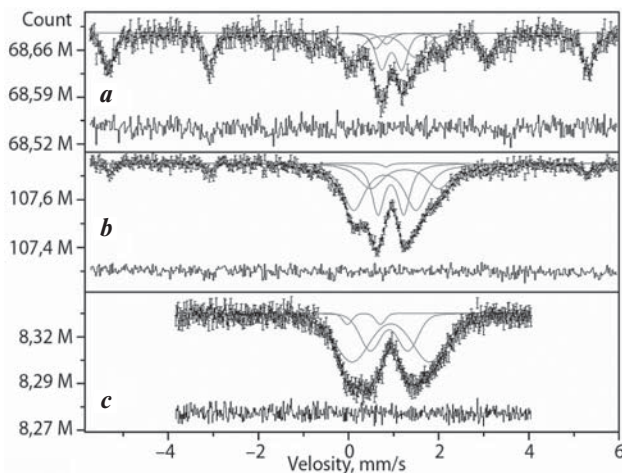


Fig. 3. Mössbauer spectra of ESR slag of ANF-6 type, room temperature:
a — 2–1 (41% Fe⁰, 59% Fe⁺²); *b* — 2–2 (8% Fe⁰, 92% Fe⁺²); *c* — 2–3 (96% Fe⁺², 4% Fe⁺³)

determined, then taken into account when processing the spectra of study samples. **Table 2** shows the parameters of the spectra after subtraction of the beryllium window subspectrum (background). Chemical shift values are indicated relatively to α -Fe.

The Mössbauer spectra of the study samples (**Fig. 3**) represent a combination of broad, poorly resolved resonance lines with a highly low effect value (about 0.1 %). In most cases, the main part of the spectrum is concentrated in its central “paramagnetic region”. For samples 2–1 and 2–2, rather narrow resonance lines corresponding to α -Fe are clearly distinguished on the spectra indicating the realization of conditions similar to equilibrium when forming this phase. In case of sample 1-1-⁵⁷Fe, it is possible to distinguish subspectrum 2 with parameters corresponding to the metal-like iron θ -carbide Fe₃C [21].

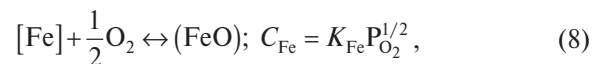
For samples 1-1-⁵⁷Fe and 1-2-⁵⁷Fe the ferromagnetic part of the spectrum has a relaxation form specific for strongly disordered iron atoms in the phases obtained under nonequilibrium conditions. Nevertheless, for almost all spectra it is possible to give satisfactory models describing subspectra by 2–4 superposition that can be unequivocally attributed either to the metallic iron derivatives, or to the iron oxygen derivatives in o.s. of +2 and/or +3. Practically for all samples (except for 2-1, Table 2), it is possible to reliably exclude the possibility of formation of fluoride iron compounds in o.s. of +2 and +3, because the observed isomeric shifts are noticeably lower than the expected for iron atoms in the fluoride environment (1.36 for Fe⁺² and 0.48 for Fe⁺³ [13, 22]).

Discussion

Owing to a considerable specific surface area of the dispersed particles of powder metal beads, as well as statistically uniform distribution over the slag volume, the

degree of their composition reaching the equilibrium, confirmed by experimental verification [6]. Thus, the proposed procedure allowed investigating the features of iron equilibrium distribution between the metallic and slag phases.

The relation of Po₂ with iron concentration in the slag expressed in its atomic fraction C_{Fe}, shown in Fig. 1 in double logarithmic coordinates turned out to be nonlinear. The result obtained is satisfactorily explained taking into account a change in the average iron o.s. (v_{Fe}) in slag at a change in Po₂. Indeed, when $v_{Fe} = +2$, which corresponds to oxide FeO of stoichiometric composition, it can be written that:



where K_{Fe} is a constant value for this slag composition at a constant temperature.

The line 4 represents this relationship (8) in Fig. 1. The tangent of an angle between the line and the abscissa axis at any point is 1/2. The tangent of the angle between the experimental curves and the abscissa axis gradually increases with increasing Po₂, prompting suggestion that that Po₂ affects v_{Fe} .

As noted above, metallurgical slags along with other condensed oxides are generally marginally non-stoichiometric, that is having a finite (but not equal to zero) homogeneity area. In a particular case, for the oxide represented by the formula FeO_x, the electroneutrality condition (2) is expressed by the equation:

$$v_{Fe} + xv_O = 0, \quad (9)$$

where v_{Fe} and v_O are o.s. of iron and oxygen, respectively, with $v_O = -2$.

The iron o.s. in the oxide phase is associated with its stoichiometric ratio by the equation:

$$v_{Fe} = 2x. \quad (10)$$

Taking into account an “electronic” component μv_i in equation (1) of the chemical potential of the slag component (*i*) leads to the following expression for a coefficient of element distribution between metal and slag:

$$K_i = a'_{(i)} / a_{[i]} e^{\frac{\mu v_i}{RT}}. \quad (11)$$

From relations (4) and (11) for $i = Fe$, the constant temperature assigned to the slag composition determining the values of A and B dimensional coefficients, at low concentrations:

$$C_{Fe} = A + B \cdot Po_2^{v_{Fe}/4}. \quad (12)$$

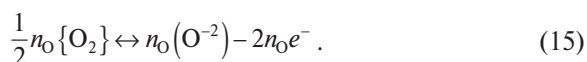
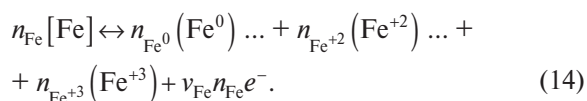
It is easy to see that relation (8) is a special case (12) and v_{Fe} reflects the value of the first-order derivative of the functions mapped by the experimental curves in Fig. 1.

Despite the fact that the assumptions on zero width of iron 4s-zone of in the slag phase and μ_o° constant for different slags are rather rough approximations, the experimental data on various slag systems correlate with the calculated dependence in the investigated range of P_{O_2} .

Based on the fact that in derivation (7) a hypothesis was used saying that it is impossible to form stable iron compounds in the system at the o.s. of +1 [4], the consistency of the data obtained in the present work with the theoretically predicted dependence indicates the correctness of the assumptions made in (7) concerning possible iron o.s. in slags. v_{Fe} value is a statistical characteristic of iron o.s. (13):

$$v_{Fe} = \frac{(0n_{Fe^0} \dots + 2n_{Fe^{+2}} \dots + 3n_{Fe^{+3}})}{(n_{Fe^0} \dots + n_{Fe^{+2}} \dots + n_{Fe^{+3}})} \quad (13)$$

The distribution of iron and oxygen between the slag and the metal can be represented as a result of redox reactions (14) and (15) involving n_O and n_{Fe} moles of the oxygen and iron, respectively, in fulfillment the electro-neutrality condition (16) taking into account the Gibbs-Duhem equation (17):



$$v_{Fe}n_{Fe} - 2n_O = 0 \quad (16)$$

$$n_O d\mu_{(O)} + n_{Fe} d\mu_{(Fe)} = 0 \quad (17)$$

The presence of “steps” on the curves (Fig. 2) corresponds to stable average iron o.s. that can be stipulated both by the predominance of the mole fraction of a corresponding o.s. in P_{O_2} interval and their equilibrium.

The average o.s. for samples can be calculated by the relation (7) on the basis of the obtained data:

$$v_{Fe} = \frac{\sum S(k) \cdot v_{Fe}(k)}{100} \quad (18)$$

where $S(k)$ is the relative area of subspectrum k , $v_{Fe}(k)$ is iron o.s. corresponding to subspectrum k in Table 2. The data obtained from the Mössbauer spectra are shown in Fig. 4.

Based on the analysis of the results obtained within each series of experiments, it can be concluded:

- all slag samples are phases of complex composition containing iron in o.s. of 0, +2 and +3 in various combinations and ratios;
- an increase in the iron content in the slag leads to a monotonous increase in the average o.s. and a decrease in the metallic iron fraction;
- average iron o.s. in the slag is mainly determined by the balance between Fe^0 and Fe^{+2} ;

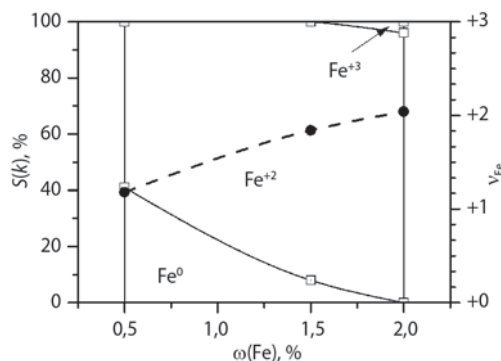


Fig. 4. Change in the relative iron content in various o.s. (squares) and the average o.s. (dots) depending on the iron content in ANF-6 slag according to Mössbauer spectroscopy data

– in samples extracted from melts immediately after adding $^{57}Fe_2O_3$, the average iron o.s. is mainly determined by Fe^0 and Fe^{+3} , and in 15 minutes most of the iron is reduced to metal reducing the average o.s. up to +0.96.

So, by Mössbauer spectroscopy method, the hypothesis has been confirmed expressed earlier about iron in o.s. Fe^0 , Fe^{+2} and Fe^{+3} slag melts and the conditions have been identified determining the ratios of these o.s.

Conclusions

Taking into account the structural peculiarities of the external iron electron shells, a kind of dependence of its average o.s. in the slag phase on P_{O_2} was proposed and it was experimentally established that a decrease in P_{O_2} from 10^{-6} to 10^{-10} Pa at 1873 K leads to a decrease in v_{Fe} by approximately a factor of 2. An increase in the iron content in a slag leads to a monotonous increase in its average o.s. and a decrease in the proportion of metallic iron.

Summary

Investigation of the change in average iron (v_{Fe}) o.s. depending on P_{O_2} and slag temperature on the basis of the use of electromotive force methods with solid electrolyte and Mössbauer spectroscopy confirmed the possibility of simultaneous presence of iron in o.s. from 0 to +3 in a slag melt. The obtained theoretical and experimental results are consistent with the concepts of slags as phases of a composition variable by oxygen, the thermodynamic description of which requires accountancy of their electronic system characteristics.

The results indicating the simultaneous presence of iron in slags in various o.s., the established relationship of P_{O_2} with the content and the average iron o.s. are of interest for the improvement of metallurgical technologies that require maintenance of a given redox potential of slag with various steel refining options, primarily for the off-furnace processing and electroslag remelting. Due to the expressness and objectivity of such information, the issues of control over slag oxidation, the content of easily

oxidizing elements in the fusion-bonded ingot are most adequately addressed.

Acknowledgement

The paper was completed with the financial support of the Ministry of Education and Science of the Russian Federation within the framework of the Agreement on granting a subsidy for the implementation of the applied scientific research on the issue with Unique identifier of the applied research and experimental development: RFMEFI57916X0134. We are thankful to D.A. Shurygin and D.K. Terekhin (JSC “RPA “CNIITMASH”) for their assistance in discussing and preparing the material for the article and conducting experiments.

REFERENCES

- Pavlov A. V. Physicochemical properties of polyvalent elements in melts and development of energy and resource saving metallurgical technologies: thesis ... Dr. Eng.: 05.16.02. Pavlov Alexander Vasilievich; Moscow Steel and Alloys Inst., Moscow, Russia (2002) 351 p.
- Cheremisina E., Shenk J. Investigation of the content hexavalent chromium occurred in slags during steel making process. *Chernye Metally*. 2018. No. 4. pp. 11–12.
- Ponomarenko A. G. The problems of thermodynamics of the phases with variable composition having collecting electronic system. *Fizicheskaya khimiya*. 1974. Vol. 48. No. 7. pp. 1668–1674; Vol. 48. No. 8. pp. 1950–1958.
- Hrapko S. A. On electronic input in thermodynamical functions of solutions. *Collection of research papers of DonNTU-2012. Metallurgy series*. Donetsk, Ukraine. 2012. No. 1(14) – 2(15). pp. 3–13.
- Mikhailov G. G., Kuznetsov Yu. S., Kachurina O. I., Chernukha A. S., J. Analysis of phase equilibriums in the system “Fe oxides – carbon – CO – CO₂”. *Vestnik Yuzhnouralskogo gosudarstvennogo universiteta. Metallurgy series*. 2013. Vol. 13. No. 1. pp. 6–13.
- Levkov L. Ya. Theoretical prerequisites and practical methods of controlling physicochemical and thermophysical processes in electroslag remelting that determine the quality of critical products: thesis ... Dr. Eng.: 05.16.02/ Levkov Leonid Yakovlevich, JSC “RPA “CNIITMASH”. Moscow, Russia (2016) 339 p.
- Yan B., Zhang J., Song Q. Thermodynamic behaviour of transition metal (Cr, Ti, Nb, V) oxides in molten slags. *Proc. VIII International Conference on Molten Slags, Fluxes and Salts, MOLTEN – 2009. Santiago, Chile*. Chapter 1. pp. 309–317.
- Hundermark R. J., Jahanshahi S., Sun S. *Proceedings IMPC 2003. Cape Town. SA*. Vol. 3. pp. 1370–1378.
- Levkov L. Ya. Oxidation-reduction modeling of electroslag remelting. *International Conference on Mathematical Modeling and Simulation of Metal Technologies MMT. Ariel, Israel*. 2000. pp. 35–37.
- Dub V. S., Levkov L. Ya., Shurygin D. A. Applications of ESR in modern energy engineering. *Proceedings of the Medovar Memorial Symposium, Kyiv, 7-10.06.2016*. pp. 39–49.
- Jonczy I., Stanek J. Phase composition of metallurgical slag studied by Mössbauer spectroscopy. *Nukleonika*. 2013. Vol. 58(1). pp. 127–131.
- Pankratov D. A. Mössbauer study of oxo-derivatives of iron in the Fe₂O₃–Na₂O₂ system. *Inorganic Materials*. 2014. Vol. 50. No. 1. pp. 82–89. DOI: 10.1134/S0020168514010154.
- Menil F. Systematic trends of the ⁵⁷Fe Mössbauer isomer shifts in (FeO_n) and (FeF_n) polyhedra. Evidence of a new correlation between the isomer shift and the inductive effect of the competing bond T–X (→Fe) (where X is O or F and T any element with a formal positive charge). *J. Phys. Chem. Solids*. 1985. Vol. 46. pp. 763–789.
- Sunayama S., Kavakami M., Goto K. S. Quick Measurement of Oxygen Potential in Steelmaking. *Tetsu-to Hagane*. 1978. Vol. 64. No. 4. pp. 12–18.
- Timucin M., Morris A. E. Phase Equilibria and Thermodynamic Studies in the System CaO–FeO–Fe₂O₃–SiO₂. *Met. Transactions*. 1970. Vol. 1. pp. 3193–3201.
- Kawakami M., Goto K. S., Matsuoka M. A. Solid Electrolyte Oxygen Sensor for Steelmaking Slags of the B. O. Converter. *Met. Trans*. 1980. Vol. 11 B. pp. 463–469.
- Yang L., Belton G. R. Iron redox equilibria in CaO–Al₂O₃–SiO₂ and MgO–CaO–Al₂O₃–SiO₂ slags. *Meta. Mat. Trans*. 1998. Vol. 29B. pp. 837–845.
- Shiro Ban-Ya Mathematical Expression of Slag-Metal Reactions in Steelmaking Process by Quadratic Formalism Based on the Regular Solution Model Faculty of Engineering. *ISIJ International*. 1993. Vol. 33. No. 1. pp. 2–11.
- Jahanshahi S., Sun S. Zhang L. Recent Developments in Physico-Chemical Characterisation and Modelling of Ferroalloy Slag Systems. *Proceedings: Tenth International Ferroalloys Congress. 1–4 February 2004. Cape Town. S.A*. pp. 316–332.
- Mikelsons J. Degree of oxidation of iron in CaO–SiO₂–FeO_n slag melts as a Function of the oxygen partial pressure of the gas phase. *Archiv für das Eisenhüttenwesen*. 1982. Vol. 53. № 6. pp. 251–265.
- Yurkov G. Yu., Fionov A. S., Kozinkin A. V., Koksharov Yu A., Ovtchenkov Y. A., Pankratov D. A., Popkov O. V., Vlasenko V. G., Kozinkin Yu. A., Biryukova M. I., Kolesov V. V., Kondrashov S. V., Taratanov N. A., Bouznic V. M. Synthesis and physicochemical properties of composites for electromagnetic shielding applications: a polymeric matrix impregnated with iron- or cobalt-containing nanoparticles. *Journal of Nanophotonics*. 2012. Vol. 6(1). pp. 061717.1–061717.21. DOI: 10.1117/1.JNP.6.061717.
- Rostovshchikova T. N., Korobov M. S., Pankratov D. A., Yurkov G. Y., Gubin S. P. Catalytic conversions of chloroolefins over iron oxide nanoparticles. 2. Isomerization of dichlorobutenes over iron oxide nanoparticles stabilized on the surface of ultradispersed poly (tetra fluoroethylene). *Russ. Chem. Bull*. 2005. Vol. 54(6). pp. 1425–1432. DOI: 10.1007/s1172-005-0422-1.