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INTERACTION OF GAS PHASES WITH ACIDIC RUST MELT AND METAL

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ABSTRACT

After ores are extracted from mines, they undergo various processing processes, after which they are smelted. The smelting process is carried out in various types of smelting furnaces and units. The working areas of these units are built of refractory materials. These refractory materials are eaten, destroyed, and fail for various reasons. One of the reasons that accelerates the erosion of refractory materials is the dross formed during the smelting process. This largely depends on the composition of the dross. The dross contains metal and non-metal oxides of various compositions and nature. Since the composition of the dross is of various nature, the mechanism of action is also different. The article clarifies the effect of dross on the working volume of the furnace during the smelting process, and proposals are put forward for its elimination.

The acid open-hearth process allows steel to be produced with a lower gas content compared to the basic process.

Introduction

Hydrogen permeability of acid steel making rusts the process of hydrogen transfer from the furnace atmosphere through acid rust into metal includes the stage of dissolution of water vapor in the rust melt without considering in detail the data available in the literature on the solubility of water vapor in the rust melt, It should be noted that they were first obtained in a study, the results of which are consistent with our recent research work [2]. The degree of acidity of the rust melt can be described by the equations of hydrogen mass transfer through the slag melt layer to the slag-metal interphase surface and the transition of hydrogen from the rust to the metal.

$$H_2O_{\text{г}}+0^{2-}_{ru.}=20H^{-}_{ru.};\ (1)$$

$$H_2O_{\text{г}}+2Si0^{4-}_{4ru.}=20H^{-}_{d.}+Si_2\ 0^{2-}_{7ru.}\ (2)$$

$$H_2O_{\text{г}}+Si_2\ 0^{6-}_{7}=20H^{-}_{ru.}+2Si0^{2-}_{3ru.}\ (3)$$

The last rust, depending on the process conditions and the degree of oxidation of the metal, can proceed in different ways. For example, the decomposition of hydroxyl into oxygen and hydrogen can proceed with the participation of iron atoms of the surface layer of the metal or without the participation of iron atoms.

In the conditions of experiments on studying the hydrogen permeability of rust melts, all the above-mentioned rustes of hydrogen movement took place [3]. Some researchers claimed that with an increase in the basicity of the rust, the hydrogen content in the steel increases, while others reported a decrease in the hydrogen concentration in the metal with an increase in the basicity of the rust melt. Therefore, in the first series of experimental melts, the effect of the basicity (CaO/SiO_2) of electric steel-making slags on their hydrogen permeability was studied. The technique was similar to that previously described in as applied to the main electric steel-making slags. With the method used for supplying the steam-nitrogen mixture (Fig. 1), which primarily washes the crucible with molten metal and rust, the gas permeability of the crucible could greatly affect the results obtained.

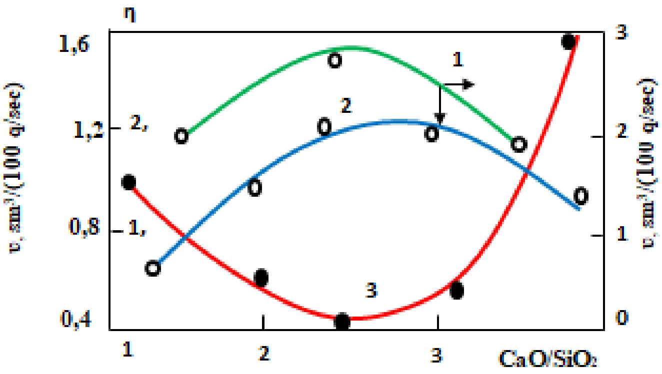

Fig. 1. The influence of the basicity of electric steelmaking rusts of the reduction period on their hydrogen permeability under industrial (1) and laboratory (2) conditions and on their viscosity (3) at 1650 ^{0} C.

In this connection, several melts were carried out to clarify the hydrogen permeability of the zirconium dioxide crucibles used. For this purpose, the molten metal in the crucible was covered with a layer of rust containing 60% SiO_2 , 25% CaO, 25% Al_2O_3 impermeable to hydrogen. A sample of the metal was taken for hydrogen, and then hydrogen was supplied to the system from a cylinder for 20 minutes. Experiments showed that the ones used for hydrogen.

Specially conducted melts with a doubled rust layer thickness showed that its hydrogen permeability also decreased by half. In other words, the hydrogen permeability of the rusts was limited by the process of hydrogen mass transfer through the rust layer [4,5].

Experiments were carried out mainly at 1650 ^{0}C and a partial pressure of water vapor in the gas phase of 150 mm Hg. The chemical composition of industrial acid open-hearth slags, selected from a 90 t furnace, is given in Table 1.

The main component of acid steelmaking rusts is silica, so it was necessary to first check the effect of its concentration on the hydrogen permeability of the rusts. As can be seen from Table 1, the silica content in the rusts we studied varied from 39.0 to 61.80%.

Table 1. Chemical composition of acidic open-hearth rust

Rust group	**Contents of components, %**								**SiO_2/ FeO+MnO**
	SiO_2	**CaO**	**FeO**	**Fe_2O_3**	**MnO**	**Cr_2O_3**	**Al_2O_3**	**MgO**	
I	39,00	4,20	36,00	1,70	15,30	1,93	0,90	0,80	0,72
	41,76	4,65	34,82	1,67	14,29	1,82	0,81	0,17	0,81
	46,80	4,70	28,80	1,20	15,00	1,80	0,80	0,17	1,03
	49,07	4,90	22,20	0,60	15,60	1,73	4,38	0,60	1,27
	54,23	4,60	16,70	0,30	17,60	1,38	4,19	0,61	1,56
	56,70	4,40	13,10	-	19,40	0,84	4,18	0,57	1,74
	59,40	4,29	11,20	-	19,60	0,74	4,00	0,62	1,92
	61,80	4,30	10,01	-	19,46	1,13	3,76	0,14	2,11
	56,70	4,40	13,10	-	19,40	0,84	4,18	0,57	1,74
	55,00	6,80	13,00	-	19,00	0,80	4,10	0,50	1,71

II	54,00	9,70	12,10	1,51	17,40	0,96	2,16	0,97	1,71
	52,00	11,70	12,00	1,50	17,30	1,00	2,10	1,00	1,68
	52,20	11,60	11,60	1,26	16,80	0,82	2,10	1,01	1,75
III	59,40	4,29	11,20	-	19,60	0,74	4,00	0,62	1,92
	57,20	4,00	11,00	-	19,00	0,74	7,00	0,60	1,90
	53,40	3,30	12,60	-	17,60	0,80	10,70	0,60	1,76
	52,20	3,10	12,00	-	17,00	0,80	13,00	0,60	1,81
	51,20	3,00	12,30	-	15,10	0,90	16,40	0,62	1,88

The silica concentration in the slag increased mainly due to ferrous oxide from manganese oxide, so Fig. 2 shows the dependence of the hydrogen permeability of the rusts on the SiO/FeO+MnO ratio [5,6]. With an increase in this ratio from 0.72 to 2.11, the hydrogen permeability of the slags decreases from 1.00 to 0.09 cm³ (100 g/min). This is explained by a significant increase in rust viscosity with an increase in the SiO_2/(FeO+MnO) ratio (Fig. 3) and a decrease in oxygen activity in the slag with an increase in the silica concentration (since SiO_2 is a strong complexing oxide), due to which the reaction of dissolution of water vapor in the rust is hindered.

$$H_2O_{\text{г}} + 0^{2-}_{d.} = 20H^{-}_{d.} \quad (4)$$

The data we obtained on the effect of the SiO_2/(FeO+MnO) ratio on the hydrogen permeability of acid rusts were later confirmed by our colleagues and explained from the point of view of thermionic emission of oxide melts. The authors of studied the work function of electrons from acid rusts that had the same chemical composition as the melts we studied.

It was found that with an increase in the SiO_2 /(FeO+MnO) ratio, the work function of electrons from rusts increases, and, consequently, the thermionic emission of the rust melt decreases:

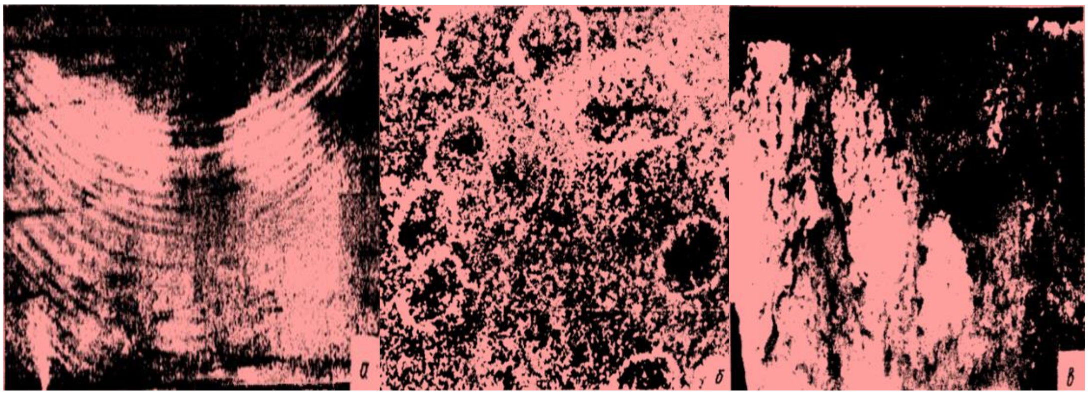

Fig. 2. Inclusions in steel 30KhGSNA. X500: a, b, aluminum additive after alloying steel with silicon; c-aluminum additive before alloying steel with silicon

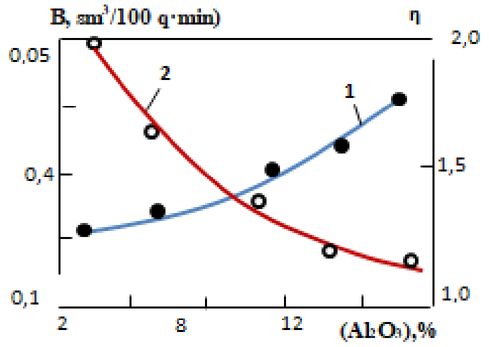

Fig. 3. Effect of Al_2O_3 on hydrogen permeability (1) and viscosity (2) of acidic open-hearth rusts at 1650 ⁰C and p_{H_2O}= 150 mm Hg.

In this connection, it is extremely important to study the effect of partial pressure of water vapor in the gas phase on hydrogen permeability of steelmaking rusts. Experiments were conducted at 1650 ^{0} C and p_{H_2O} in the gas phase equal to 55, 100, 170 and 260 mm hg**.**

The experimental data (Fig. 4 and Table 2) allowed us to establish a linear dependence of the hydrogen permeability of a rust of a given composition on the square root of the partial pressure of water vapor in the gas phase.

Due to the fact that the solubility of water vapor in rusts changes little within the limits of temperature fluctuations during open-hearth smelting [7] it can be assumed with a certain error that the difference C_1-C_2 in the equation ($\upsilon_H = \beta_H S(C_1 - C_2)$) remains constant for a certain point in time when the temperature changes. Then, using the experimentally established dependence of the hydrogen permeability of the rust on temperature, it is possible to estimate the apparent activation energy of the hydrogen permeability process.

To do this, we represent the equation ($\upsilon_H = \beta_H S(C_1 - C_2)$) in the following form:

$$\upsilon_H = AB_0\, e^{-E/RT}(C_1 - C_2) \quad (7)$$

$$\lg = \upsilon_H = A_0 - B_0/T \quad (8)$$

Where,

$$A_0 = \lg AB_0 \quad (9)$$

$$B_0 = E/R \lg e = E/4{,}575 \quad (10)$$

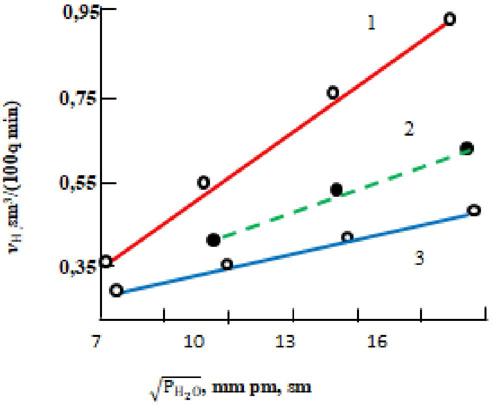

Fig. 4. The influence of p_{H_2O} in the furnace atmosphere on hydrogen permeability of acidic rusts at 1650 ^{0}C
1 – rust, 2 – s rust; 3 – rust, 6 (see table 2).

In this case, the tangent of the angle of inclination of the straight line to the abscissa axis (Fig. 5) will characterize the apparent activation energy of the rust hydrogen permeability process. For the rust containing 49.0% silica, this value was equal to 56.8 kcal/mol, and for the melt with 54.20% silica, 74.6 kcal/mol.

Thus, the study of the hydrogen permeability of unstirred rusts showed that the limiting link in the process is the mass transfer of hydrogen in the rust layer, determined mainly by the viscosity of the latter [8] .

The rate of hydrogen transition from the gas phase through the slag to the metal is expressed as the rate of the first-order reaction and is proportional to the square root of the partial pressure of water vapor in the furnace atmosphere:

$$\upsilon_H = K_{OH^-}(OH^-) = K_{OH^-}\sqrt{K_{H_2O}}(O^{2-})P_{H_2O} = K_H\sqrt{P_{H_2O}} \quad (10)$$

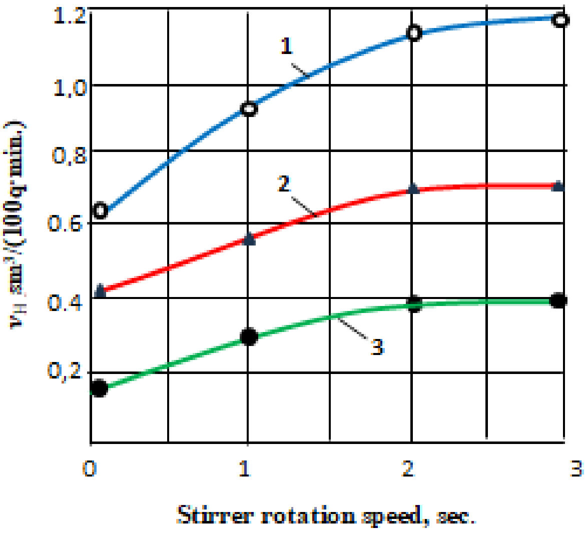

Fig. 5. Effect of mixing intensity on hydrogen permeability of rust with different compositions:

1 - 52,2% SiO_2; 14,6 % CaO; 11,6 % FeO; 16,8 % MnO; 2 – 49,0 % SiO_2; 4,9 % CaO; 22,2 % FeO; 15,6 % MnO; 3 – 59,4 % SiO_2; 4,3 % CaO; 1,1-2,0 % FeO; 19,6 % MnO

A similar phenomenon was observed [9] when stirring slag in an open-hearth furnace at different periods of melting with a steel stirrer. When stirring relatively calm rust at the end of the melting period, the hydrogen content in the metal increased from 3.6 to 4.3 sm³ /100 g, and stirring at the beginning of pure boiling of mobile rust with a stirrer did not lead to an increase in the hydrogen content in the metal.

When comparing the rust stirring power during the boiling period (υ_C = 0.24 % S/h) in an open-hearth furnace with the maximum power spent on slag stirring in our experiments, it turned out that the stirring power in our case was somewhat lower than the ruts stirring power in an open-hearth furnace at a carbon oxidation rate of 0.24 %/h.

From the above it follows that with intensive rust stirring, the rate of hydrogen mass transfer in it increases so much that it begins to exceed the rate of processes occurring at the interfaces of the rust melt with the gas and metal phases. In other words, the process changes from a diffusion mode to a kinetic mode.

Experiments with stirred slags, conducted by us in crucibles of a special shape [10], showed that the change in the total rate of hydrogen transition from the gas phase through the slag into the metal is proportional to the change in the specific surface area at the rust-metal phase boundary. In this case, the rate of hydrogen transition from the furnace atmosphere through the rust into the metal can be expressed as the rate of a second-order reaction:

$$\upsilon_H = K_{OH^-}(OH^-)^2 = K_{OH^-}K_{H_2O}(O^{2-})P_{H_2O} = K_H P_{H_2O}, \quad (11)$$

i.e., υ_H is proportional to the partial pressure of water vapor in the gas phase.

The latter was confirmed in experiments conducted with stirred slag II (see Table 2) at different P_{H_2O} in the furnace atmosphere. The experiments showed that υ_H in this case changes proportionally to P_{H_2O}

υ_H sm^3 /(100 q·min)……. 1,13 0,72 0,34

P_{H_2O}, mm pт.st……………..150 100 50

With an increase in the MnO/FeO ratio from 0.50 to 1.85, the hydrogen permeability of rusts increases, and a further increase in this ratio is accompanied by a decrease in the value of hydrogen permeability of slags.

With an increase in the content of manganese oxide instead of ferrous oxide, there is an increase in the solubility of hydrogen in rusts, since the strength of the bond of oxygen anions with manganese ($r_{Mn^{2+}}$ = 0,91 Å) is less than with iron ($r_{Fe^{2+}}$ = 0,83 Å), and the reaction $H_2O_r+O^{2-}$ = $2OH^-_{ru.}$ occurs faster.

A decrease in the hydrogen permeability of rusts with an increase in the MnO/FeO ratio from 1.85 to 2.42 can be explained based on the fact that the transition of hydrogen from rust to metal is accompanied by reactions.

$$2(OH^-) + (Fe^{2+}) = [Fe] + 2[O] + 2[H] \quad (12)$$

$$2(OH^-) + (Mn^{2+}) = [Mn] + 2[O] + 2[H] \quad (13)$$

using the "narrowing" method when processing experimental data on the hydrogen content in the rust and metal, he determined the equilibrium constants of the latter reactions (12) and (13). The values of the changes in the isobaric potential under standard conditions for these reactions are expressed respectively

$$\Delta G = 118000 - 61{,}5T \quad (14)$$

$$\Delta G = 192800 - 91{,}0\,T \quad (15)$$

These equations allow us to conclude that the reactions of hydrogen transfer from rust to metal are sharply endothermic, and the reaction involving iron cations is of greatest importance in the process of hydrogen transfer from rust to metal, because it requires less energy. It is evident from this that at a high value of the MnO/FeO ratio (from 1.85 and above), hydrogen transfer from rust to metal occurs mainly due to manganese cations. This process requires a large energy expenditure, therefore, the hydrogen permeability of rusts, starting from the MnO/FeO ratio of 1.85, decreases. After laboratory studies, the effect of the rust regime on the behavior of hydrogen in the metal of acid open-hearth and electric steelmaking furnaces under industrial conditions was studied. The smelting was carried out using an active and silicon-reducing process. The open-hearth furnaces at both plants (Baku Steel Company) had the same capacity (90 t) with a hearth area of 30.0 and 28.0 m2 and were heated with fuel oil. The electric furnace had a capacity of 5 t.

Silicon reduction smelts were carried out by a duplex process (the main one was acid open-hearth furnaces). The data on these smelts are given in Table 2 (the first six smelts). The last four smelts (see Table 3) were carried out by an active process on a solid charge using 3.5% recycled rust and 0.5% iron ore. The smelts presented were carried out by an active process on a solid charge without the use of recycled rust.

During each smelt, seven metal samples were taken for hydrogen with simultaneous rust samples taken to determine the chemical composition. The metal samples after quenching in water were placed in eudiometric vessels with alcohol, where they were kept for five days. Samples of metal and rust were started to be taken 1 hour before the complete melting of the charge. Figure 6 shows the effect of the duration of the melting period on the hydrogen content in the metal after melting, as well as the effect of the SiO_2 (FeO + MnO) ratio in the rust taken 1 hour before the complete melting of the charge on the increase in the hydrogen content in the metal during the last hour of the melting period. Comparing the effect of these two factors, it can be seen that the hydrogen content in the metal after melting is mainly determined by the chemical composition of the slag, on which the viscosity and hydrogen permeability of the latter depend.

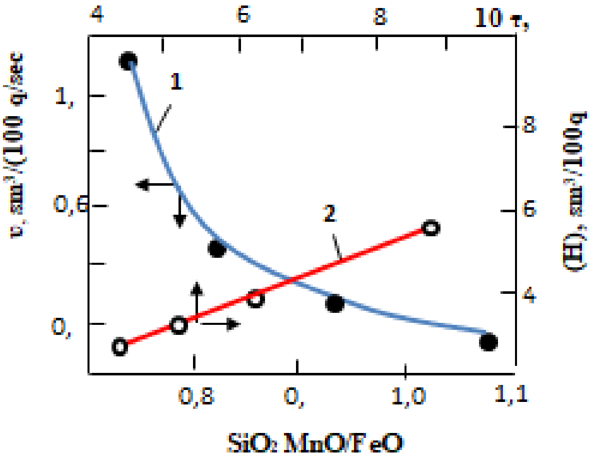

Fig. 6. The effect of the SiO_2 (FeO + MnO) ratio in the rust collected 1 hour before melting on the increase in the hydrogen content in the metal during the last hour of the melting period (1) and the effect of the duration of the melting period on the hydrogen content in the metal (2)

Table 2. Hydrogen behavior in metal during melting carried out by silicon-reducing and active processes using recycled rust.

Melt number	**Sample number**	**[C], %**	**[MH], %**	**Rust composition, %**						**(H), sm³/100q**	**υ, sm³/ (100 q/sec.)**
				SiO_2	Al_2O_3	FeO	CaO	MgO	MnO		
1	1	0,94	0,14	56,30	5,34	15,67	3,56	0,17	16,77	2,60	0,18
	2	0,46	0,25	57,54	4,54	12,48	3,73	0,14	19,47	2,48	
	3	0,33	0,25	58,80	4,32	10,94	4,14	0,15	19,42	2,70	
	4	0,36	0,35	60,56	4,08	9,86	3,77	0,16	19,44	3,90	
2	1	1,04	0,12	50,93	5,50	21,18	4,41	0,12	13,67	4,63	0,14
	2	0,44	0,31	57,37	3,92	12,48	4,36	0,13	18,91	4,18	
	3	0,36	0,27	61,34	3,44	10,15	3,40	0,13	18,91	3,09	
	4	0,36	0,45	61,46	3,04	9,72	4,02	0,14	17,84	4,54	
3	1	0,90	0,28	55,96	4,13	13,78	7,36	0,12	15,75	3,91	0.19
	2	0,36	0,30	59,41	3,10	10,59	4,64	0,13	18,62	3,26	
	3	0,25	0,27	61,74	3,32	10,61	4,13	0,13	15,24	2,84	
	4	0,27	0,27	60,80	3,76	10,01	4,30	0,14	18,46	4,40	
4	1	0,96	0,07	50,82	4,32	19,81	5,02	0,13	17,84	5,02	0,11
	2	0,45	0,16	57,52	4,40	13,54	5,18	0,15	17,91	2,90	
	3	0,35	0,23	60,02	4,30	12,33	4,70	0,13	17,52	2,70	
	4	0,38	0,50	59,92	4,24	12,19	4,58	0,14	18,11	4,30	
5	1	1,01	0,10	54,20	5,82	16,68	7,41	0,15	13,37	3,50	0,15
	2	0,47	0,29	56.08	4,18	13,06	5,83	0,14	19,03	2,81	
	3	0,32	0,20	58,32	4,46	10,83	5,65	0,14	19,61	2,80	
	4	0,33	0,31	58,48	4,48	10,60	5,77	0,13	19,59	4,06	
Samples were taken: 1 - after melting; 2 - at the end of ore boiling; 3 - at the end of clean boiling; 4 - before tapping.											

In an acid electric furnace, due to the lower content of water vapor in the gas phase, the concentration of hydrogen in the metal is significantly lower than in open-hearth steel. But even under these conditions, the rust is not a complete insulator of the metal from the hydrogen-containing atmosphere. Based on our data on the study of the behavior of hydrogen in the metal bath during 60 melts in an acid electric furnace, 14 of which are described in detail, the following pattern was revealed for the melting period.

Conclusions and Discussions

1. The reduction in the causticity of the pulp is reduced by properly regulating the amount of basic and acidic oxides in its composition

2. As a result of our research, it was determined that the pulp has a low pickling effect when its content is SiO_2 /CaO<1.2

3. The results of the analyses also allow us to say that this ratio directly depends on the amount of impurities in the pulp

4. The transfer of hydrogen from the furnace atmosphere to the metal through the pulp was also studied as a result of the research

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