PHYSICAL AND CHEMICAL BACKGROUND OF SOLID-PHASE OBTAINING OF Fe - Cr LIGATURE BY GAS-CARBOTHERMIC REDUCTION

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RESUME

Thermodynamic analysis of carbothermic and complex Cr_2O_3 reduction was realized on the basis of the original procedure at temperatures that exclude charge melting. The kinetics of Fe and Cr reduction from oxide phases by carbon alone and in conjunction with gases was studied. The intensification of Cr_2O_3 reduction with the involvement of Fe_{met} was confirmed and ideas about the mechanism of the Fe_{met} influence was developed.

1. INTRODUCTION

The results of numerous studies [1-9] indicate a high efficiency of Fe and Cr extraction from ore materials by gas-carbothermic (complex) reduction. This process can be realized at moderate temperatures without charge melting. We have shown [9-11] that complex reduction of Fe from oxide phases has been developed at 1173K strongly intensified with the increase in temperature (Fig.1).

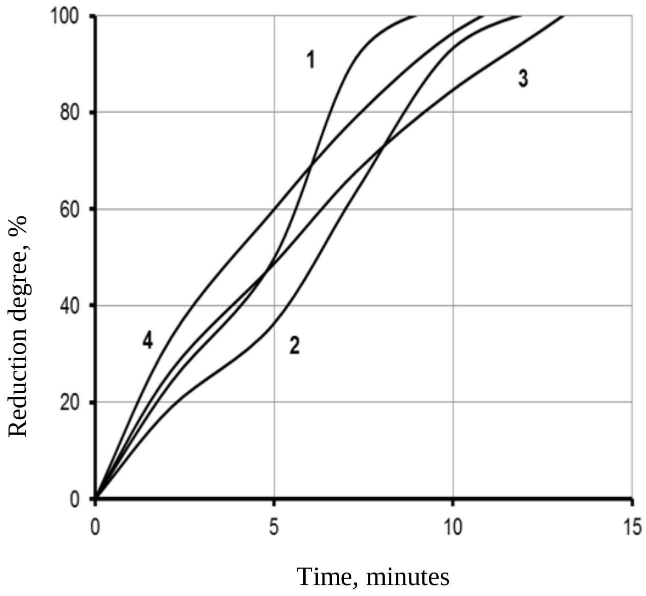


Fig. 1. Kinetics of complex reduction of Fe_2O_3 with graphite (1.2) and charcoal (3.4) at 1000 °C in a stream of 75% H_2 + 25% CO; 2, 3 - without additives; 1, 4 - 1% Na_2CO_3.

The level of thermodynamically allowed starting temperature of carbothermic Cr_2O_3 reduction is slightly higher than that for the previously mentioned iron oxides. Purely carbothermic and complex Cr_2O_3 reduction in the flow of CO can be represented by a set of different reactions. In this paper, to describe the first stage of the process reactions the following ones were chosen:

$$1/3Cr_2O_3 + CO + 4/9C = 2/9Cr_3C_2 + CO_2 \quad (1)$$

$$C + CO_2 = 2CO \quad (2)$$

They were used to determine the thermodynamically allowed starting temperature of Cr_2O_3 reduction (Tr) at different pressures of carbon-containing gases.

2. EXPERIMENT

Analyzed system is constituted by three components (K) and consists of four phases (F). Therefore, according to the phase rule (V = K+ 2 - F), it has one degree of freedom (V). When pressure of carbonaceous gases ($P_{CO} + P_{CO2} = \alpha$) is predetermined equilibrium in the system occurs at a single well-defined temperature (Tr). The equation for calculation of its value can be obtained by the following conversion of equilibrium constants expressions of reactions (1) and (2):

$$K_1 = \frac{P_{co_2}}{P_{co}}; \quad K_2 = \frac{P^2_{CO}}{P_{CO_2}} = \frac{P_{CO}}{K_1}, \quad \text{so} \quad P_{co} = K_1 \cdot K_2; \qquad (1)$$

$$K_1 = \frac{P_{CO_2}}{P_{CO}} = \frac{(\alpha - P_{CO})}{P_{CO}} \text{ ,so } \qquad P_{CO} = \frac{\alpha}{(1 + K_1)} . \qquad (2)$$

Equating the two expressions of P_{CO}, we obtain an equation which allows calculating the equilibrium temperature of the system corresponding to the beginning of Cr_2O_3 reduction to Cr_3C_2 at different pressure $P_{CO} + P_{CO2}$:

$$\alpha = K_1 \cdot K_2 \cdot (1 + K_1) \qquad (3).$$

It can be determined on the basis of previously presented equation [11,12]

$$\alpha = \exp\left(a_0 + \frac{a_1}{T}\right) \cdot \exp\left(в_0 + \frac{в_1}{T}\right) \cdot \left[1 + \exp\left(a_0 + \frac{a_1}{T}\right)\right] \qquad (4),$$

a_i and b_i stand for the numerical values of the temperature dependence of lnKp of reactions (1) and (2), respectively.

The required equations have been received by the program HSC, version 5.0.

$$\ln K_1 = -\frac{9144,5}{T} + 0.2913 \qquad (5)$$

$$\ln K_2 = -\frac{19859}{T} + 20.549 \qquad (6)$$

3. RESULTS

The results of the calculation are shown in table1.

Table 1. Thermodynamically allowed starting temperature of Cr_2O_3 reduction

Reduction type	$\alpha = (P_{CO} + P_{CO_2})$	$\beta = (P_{H_2O} + P_{H_2})$	Temperature of reduction stage, K	
			$Cr_2O_3 \rightarrow Cr_3C_2$	$Cr_2O_3 \rightarrow Cr_7C_3$
Carbothermic reduction and those in CO stream	1	-	1391,56	1581,42
	0.75	-	1372,63	1559,13
	0.5	-	1346,90	1528,86
	0.25	-	1304,81	1479,56
Complex reduction in H_2 stream	0.75	0.25	1372,55	1559.14
	0.5	0.5	1346,78	1528,83
	0.25	0.75	1304,89	1479,43

Ratio obtained above allows determining the equilibrium composition of the gas phase at Tr $P_{co} = \alpha/(1+K_1)$, which in turn provides an opportunity to calculate the value $P_{co_2} = \alpha - P_{co}$. The same result can be obtained based on the expression of K_2. Denoting Pco by X, we get the estimated equation:

$$K_2 = \frac{X^2}{(\alpha - X)} \text{ или } X^2 + K_2 \cdot X - K_2 \cdot \alpha = 0 \qquad (7)$$

It should be noted that the equation (7) provides the ability to calculate the equilibrium level (2), both above and below the level of the temperature Tr.

Calculation of the equilibrium composition of gas phase in the reaction (1) at temperatures above Tr is significantly different. At these conditions free carbon is not involved in the equilibrium of this reaction and it should be transformed to the following:

$1/3Cr_2O_3 + 17/9CO = 2/9Cr_3C_2 + 13/9CO_2$ (8)

Calculated equation can be obtained by converting the expression of the equilibrium constant

$$K_3 = P_{CO_2}^{13/9} / P_{CO}^{17/9} = \frac{(\alpha - X)^{13/9}}{X^{17/9}} \text{ or } \qquad K_3^{9/13} = \frac{(\alpha - X)}{X^{17/13}}$$

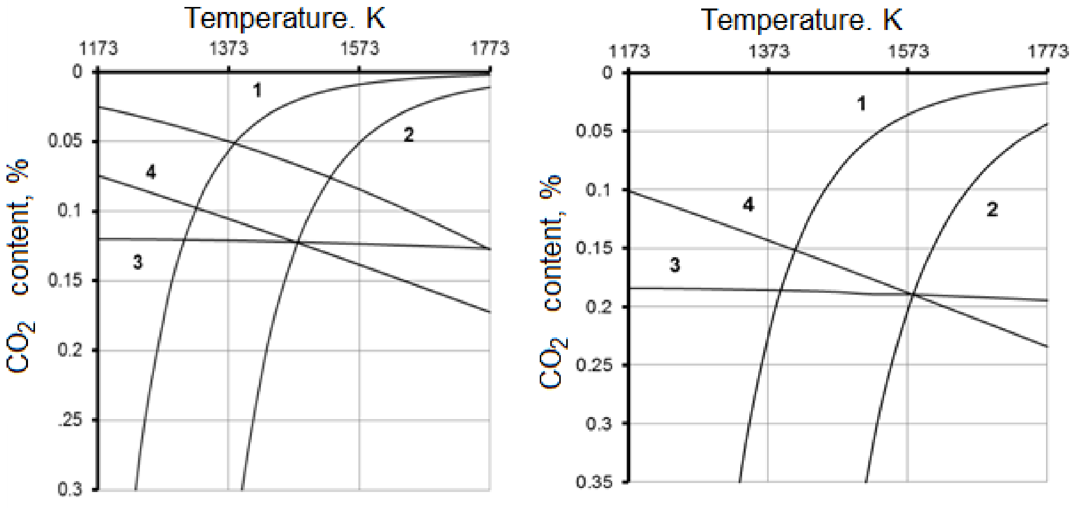
The value of $X = P_{CO}$ is determined on the basis of equation

$$X + K_8^{9/13} \cdot X^{17/13} - \alpha = 0 \qquad (9)$$

The equilibrium constant at desired temperature can be found by the equation:

$$\ln K_8 = -\frac{278.26}{T} - 8.8669 \quad (10)$$

Calculated results of the equilibrium composition of the gas phase in the reaction (8) above Tr are partially illustrated in Figure 2 (equilibrium in Cr – O - C – system at α = 0,25; α = 1,0).



a) b)

Fig. 2. The equilibrium composition of the gas phase in the Cr - O - C system at α = 0,25 (a) and α = 1,0 (b):
1 - gasification C+CO_2; 2 - gasification Cr_3C_2 + CO_2;
3 – reduction of $Cr_2O_3$to Cr_3C_2;4 - reduction of Cr_2O_3 to Cr_7C_3.

The entry to the second process step ($Cr_2O_3 \rightarrow Cr_7C_3$), where the solid reduction agent is carbide Cr_3C_2, can be described by the following reactions

$1/3\ Cr_2O_3 + CO + 2/5Cr_3C_2 = 4/15Cr_7C_3 + CO_2$ (11) $\quad \ln K_{11} = -\frac{10006}{T} + 0.0665$

$7/5Cr_3C_2 + CO_2 = 3/5Cr_7C_3 + 2CO$ (12) $\quad \ln K_{12} = -\frac{21780}{T} + 20.031$

The algorithm for determination of reduction starting temperature coincides with one shown above. It allows presenting the equation to calculate Tr as

$$\alpha = K_{13} \cdot K_{14} \cdot (1 + K_{13}) \quad (13)$$

The results of Tr determination in carbon containing gases at different pressures are shown in Table 1. The equilibrium compositions of the gas phase for reactions (13) and (14) are represented in Figure 2.

At temperatures above T_r reaction is transformed as follows:

$1/3Cr_2O_3 + 11/7CO = 2/21Cr_7C_3 + 9/7CO_2$ (14)

Denoting P_{CO} by X and transforming the equilibrium constant of this reaction to the formula

$K_{14} = \frac{(\alpha - X)^{9/7}}{X^{11/7}}$ we obtain the equation $X + K_{14}^{7/9} \cdot X^{11/9} - \alpha = 0 \cdot$

Equilibrium compositions of the gas phase are shown in Figure 2 being defined on the basis of this equation at different values of **α.**

The initial stage of complex chromium oxide reduction in a hydrogen stream or with a mixture of H_2 - CO can be described by a set of reactions (1) and (2) together with the reactions

$H_2O + CO = H_2 + CO_2$, $\quad K_{15} = \frac{P_{H_2} \cdot P_{CO_2}}{P_{H_2O} \cdot P_{CO}}$ (15) $\quad \ln K_{15} = \frac{3705.5}{T} - 3.4361$

$1/3\ Cr_2O_3 + H_2 + 4/9C = 2/9Cr_3C_2 + H_2O$, $\quad K_{16} = \frac{P_{H_2O}}{P_{H_2}}$ (16) $\quad \ln K_{16} = -\frac{12852}{T} + 3.7293$

The latter together with reaction (2) adequately describes the link of steam gasification of $C_{\mathbf{solid}}$. The feature of this unit is characterized by the fact that hydrogen formation is accompanied by the appearing of CO-CO_2 mixture, the ratio of which depends on the temperature and the proportion of carbon- and hydrogen-containing gases in the reaction mixture.

The calculation of thermodynamically allowed temperature of the complex Cr_2O_3 reduction was made in terms of the total pressure of four reactive gases $P_{\sum} = 1$ (in relative units). The problem is solved while maintaining the previously received symbols $P_{\mathbf{CO}} + P_{\mathbf{CO2}} = \alpha$ by the following transformations:

$$K_{16} = \left(\frac{P_{CO_2}}{P_{CO}}\right) / \left(\frac{P_{H_2O}}{P_{H_2}}\right) = \frac{K_1}{K_{15}} \quad \text{and} \quad K_1 = K_{15} \cdot K_{16} \cdot$$

Taking into account the relation (3) we obtain the estimated equation

$$\alpha = K_2 \cdot K_{15} \cdot K_{16} \cdot (1 + K_1) \tag{17}$$

Based on it we find the starting temperature of complex Cr_2O_3 reduction to carbide Cr_3C_2 with hydrogen acting in the process:

$$\alpha = \exp\left(в_0 + \frac{в_1}{T}\right) \cdot \exp\left(c_0 + \frac{c_1}{T}\right) \cdot \exp\left(d_0 + \frac{d_1}{T}\right) \cdot \left[1 + \exp\left(a_0 + \frac{a_1}{T}\right)\right] \tag{18}$$

the subscripts **c** and **d** denote values corresponding to the numerical expression ln Kp = f (T). Tr for different values α is given in Table 1. These naturally coincide with the results presented earlier. This is because the equilibrium in connected units (1) and (2) at the fixed value of $\boldsymbol{\alpha}$ is invariant. In turn, the equilibrium state of a complex Cr_2O_3 reduction involving hydrogen set up only at the equilibrium of all parts of the reacting system.

Ways of determining equilibrium gas composition in reactions (1), (2) and (8) and the data obtained were previously discussed. The equilibrium composition of the gas phase in reaction (15) can easily be found by the following transformation:

$$K_{15} = \frac{P_{H_2O}}{\beta - P_{H_2O}}, \qquad P_{H_2O} = \frac{\beta}{1 + K_{15}} \quad (19), \qquad \beta = 1 - \alpha$$

At temperatures exceeding Tr unit of gaseous Cr_2O_3 reduction to carbide Cr_3C_2 should be presented in the form of

$1/3\ Cr_2O_3 + H_2 + 8/9CO = 2/9\ Cr_3C_2 + H_2O + 4/9CO_2$ (20) $\ln K_{22} =$ -3983.8/T – 5.4307.

It is one of three interrelated reactions - (8), (16) and (20). Under the fixed conditions (temperature level, total pressure of reactive gases ($P_{\sum}$) and the ratio of α/β) analyzed system reaches common equilibrium point invariantly. According to Pco and Pco_2 values as defined earlier on the basis of the reaction (8), we determine the equilibrium partial pressures of hydrogen and water vapor:

$$K_{20} = \left(P_{H_2O} \cdot P_{CO_2}^{4/9}\right) / \left(P_{H_2} \cdot P_{CO_2}^{8/9}\right), \quad \frac{P_{H_2O}}{P_{H_2}} = K_{20} \cdot \frac{P_{CO}^{8/9}}{P_{CO_2}^{4/9}} = A, \quad \frac{P_{H_2O}}{\beta - P_{H_2O}} = A, \text{ so}$$

$$P_{H_2O} \cdot (1 + A) = \beta A \quad и \quad P_{H_2O} = \frac{\beta \cdot A}{1 + A} \cdot$$

Temperature level of the second phase of Cr_2O_3 reduction can be fined in the same way. The results are illustrated by Figure 3.

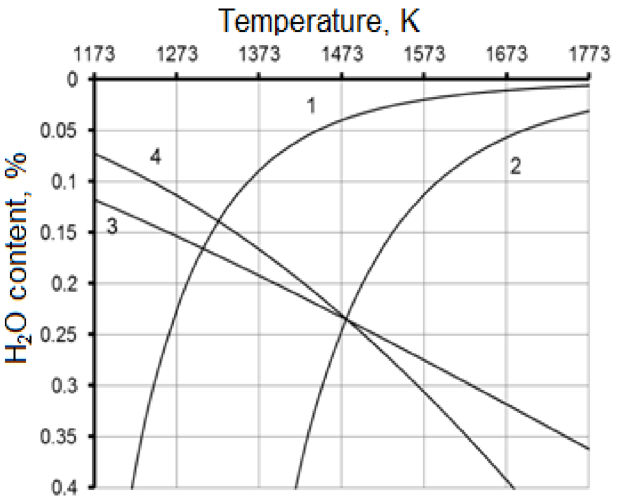


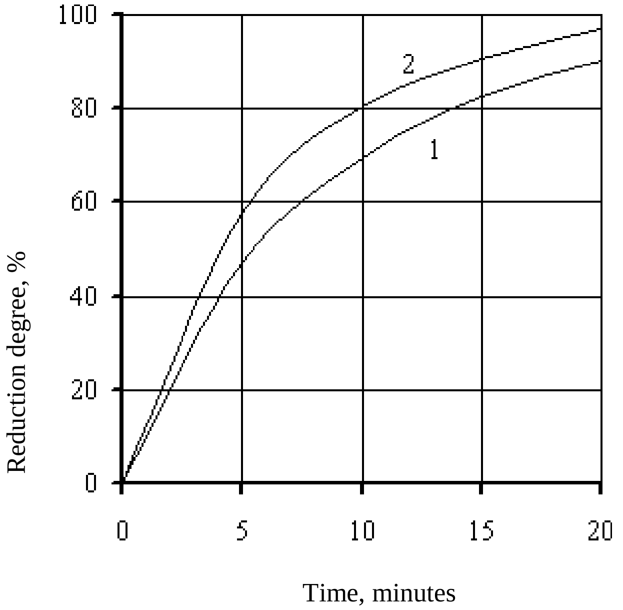
Figure 3. The equilibrium composition of the gas phase in the Cr - O - C – H -system for β = 0,75:
1 – gasification: C+ H2O;
2 – gasification: $Cr_3C_2 + H_2O$;
3 – reduction of Cr_2O_3 to Cr_3C_2;
4 - reduction of Cr_2O_3 to Cr_7C_3.

4. DISCUSSION

Kinetic studies [7,14] have shown that the transition from carbothermic to complex reduction of Cr_2O_3 by C_{solid} and Cr_3C_2 leads to significant intensification of the process. Experimental data are presented in Figure 4.

Joint reduction of chromium and iron oxides also showed that the presence of Fe_{met} significantly accelerates the reduction of oxide phases. Positive action of iron on the velocity of interaction of Cr_2O_3 with higher chromium carbide was confirmed in our study [15]. It is essential that the metal additive not only accelerates the process at 1573 and 1673K, but also initiates oxide reduction at 1473K which does not occur in the absence of $Fe_{met.}$ (Fig. 5 and 6).

The mechanism of intensifying action of iron can be disclosed based on the results of studies [16, 17]. It is well known [18] that iron is practically insoluble in Cr_3C_2. Therefore, the formation of this carbide during Cr_2O_3 reduction occurs by sided diffusion of mainly carbon and chromium into particles of metallic iron and droplets of carbon-iron melt. Carbide looses carbon, its structure becomes friable. The phase restructuring $Cr_3C_2 \rightarrow Cr_7C_3$ proceeds. The resudual carbide can dissolve up to 60% of Fe. There are conditions for counter-diffusion of iron and chromium atoms to form a mixed carbide $(Cr,Fe)_7C_3$ and Fe - Cr – C - solution. This process of interdiffusion also develops in the case of the primary appearance of Cr_7C_3 in the process of chromium oxide reduction with carbon. It must be noted that Cr_7C_3 can be a metastable phase at a stable conditions for Cr_3C_2. This may cause accelerating effect of metallic iron supplements during Cr_2O_3 reduction by carbon at 1573K (Fig. 6b) and by Cr_3C_2 at 1473K, when the process does not get development at additive absence (Fig. 5).



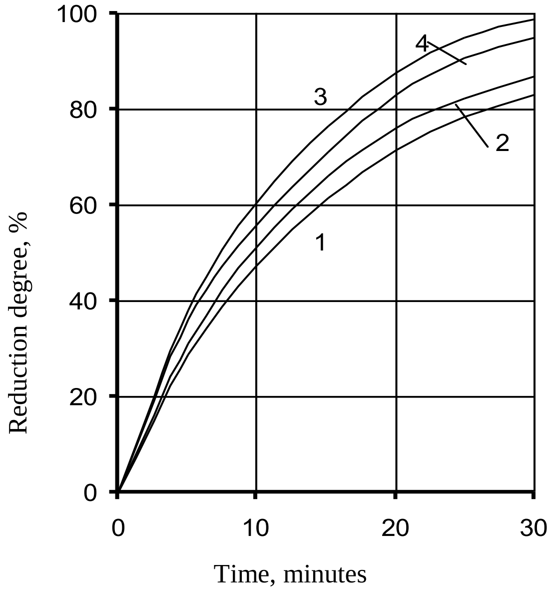


Fig. 4a. Kinetics of Cr_2O_3 reduction by Cr_3C_2 carbide at 1673K
1 – in Ar stream; 2 - in H_2 stream.

Fig. 4b. Kinetics of carbothermic (1) and integrated reduction (2-4) of Cr_2O_3 at 1573K and atomic ratio C /O = 1.44 in the ore.
1 - in a stream of argon; 2 - CO;
3 - H_2; 4 - 75% H_2 + 25% CO.

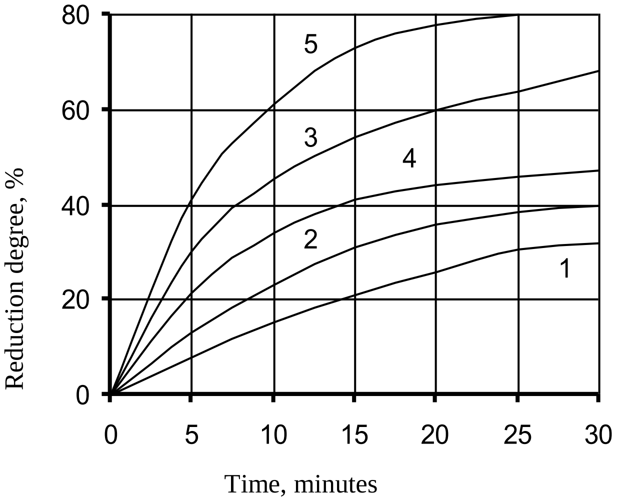
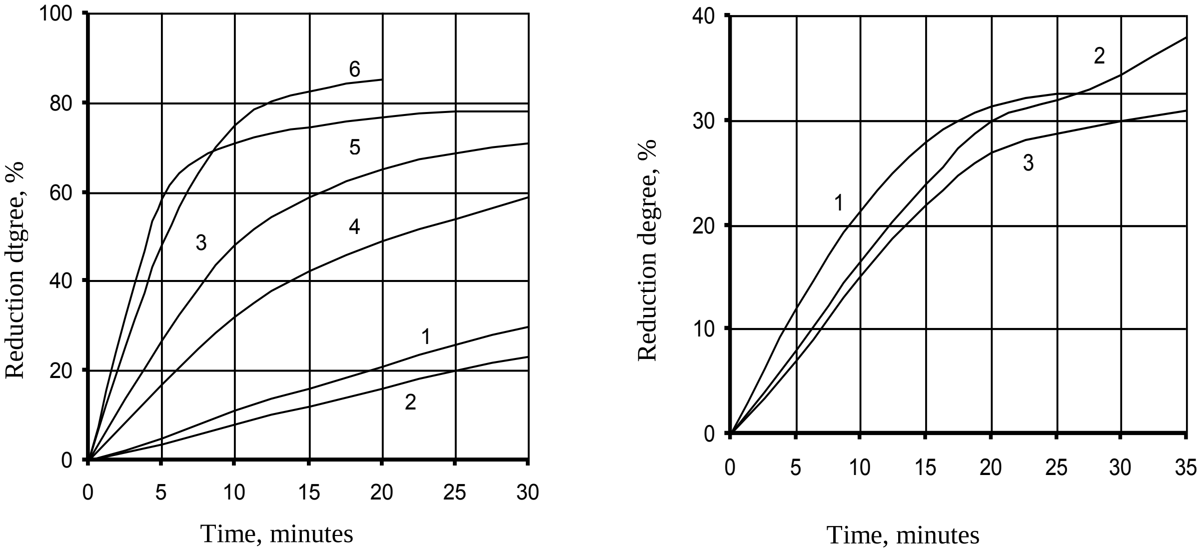


Figure 5. Kinetics of Cr_2O_3 reduction by carbide Cr_3C_2 without additives (2.4) and in the presence of metallic iron (1,3,5) at the atomic ratio C/O = 1.8 and Fe/Cr = 1
1 - 1473K; 2.3 - 1573K; 4.5 - 1673K.



a)

b)

Figure 6. The effect of metallic iron additives on the kinetics of Cr_2O_3 reduction by graphite
(a) - the atomic ratio of C/O = 1, and Fe / Cr = 1;
1.2 - 1473K; 3.4 - 1573K; 5.6 - 1673K; 1,3,5 - without Femet; 2,4,6 - in the presence of Femet;
(b) - at 1573K and the atomic ratio of C/O = 0.5;
1 - without Femet; 2 - with the addition Femet (Fe/Cr = 1);
3 - with the addition of Al_2O_3 and Femet.

Formation of mixed carbide and Fe-Cr - solution reduces the activity of the reduction products, accelerating reduction and increasing the depth of its development (curve 6, Figure 6). It does not exclude the involvement of $(Cr,Fe)_7C_3$ in the oxygen removal from the oxide phase and mixed carbide $(Cr,Fe)_{23}C_6$ formation.

The proposed intensification mechanism of Cr_2O_3 reduction by metallic iron is consent with the results of experiments when the charge contained both additives of Femet. and Al_2O_3. Kinetic curves 2 and 3 (Figure 6b) show that the presence of alumina does not significantly increase the velocity of first stage of the process. However, in the final period the picture changes when free carbon is low and Cr_3C_2 take part in reduction. Inert diluent complicates solid phase diffusion and greatly slows the reduction process.

Significant intensification of chromium reduction as well as the deepening of the process was confirmed experimentally by addition to charge of deep enriched magnetite concentrate instead of metallic iron [14]. Therefore, the presence of metallic iron and iron oxide is a guarantee of deep reduction of chromium oxide and simultaneously provide a significant decrease of carbon concentration in the metal product.

5. CONCLUSIONS

The results of thermodynamic and kinetic researches shown above indicate the availability of physical and chemical preconditions for the development of technology of ferrous-chromium alloys production in the solid phase. The resulting product can be used as the dope in the high grades steel smelting process.

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