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THEORETICAL AND EXPERIMENTAL JUSTIFICATION OF THE SOLID-PHASE REDUCTION OF CHROMIUM AND IRON FROM THEIR OXIDES

Abstract. Obtaining high-quality steel grades amid growing shortages of mineral and energy resources poses an important challenge for the metallurgical industry: improving existing technologies and developing new ones for producing alloying materials using substandard ores and waste. Solid-phase reduction (SPR) technology is a promising approach that enables sponge ligatures to be obtained from complex charges at temperatures below their melting points. This reduces energy costs and ensures a lower content of harmful elements in the metal, particularly sulfur and, under certain conditions, phosphorus. The technological features of SPR distinguish it from traditional ferroalloy production processes. This work uses an approach to the thermodynamic study of the Cr-O-C system that reflects the prevailing direction of the solid-phase reduction mechanism of chromium oxide by carbon. In this case, the process mainly occurs in the vapor-gas phase, with the gas phase (CO-CO_2) playing a decisive role in connecting the solid reagents.It has been found that further decarburization of products from the solid-phase co-reduction of chromium and iron is possible through additional thermochemical treatment of the reduction product. The reduction of carbon by treating the sponge ligature with a gas mixture of H_2 – H_2O or Ar – H_2O at a temperature of 1273 – 1373 K and H_2O concentration of 1 – 2% for 25 – 40 minutes has been scientifically substantiated and experimentally confirmed.

Keywords: solid-phase reduction, carbothermic reduction, carbide formation, chromium oxide, chromium carbide, physicochemical properties, Gibbs energy.

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Introduction

New technologies for producing sponge alloying materials have been developed and are being implemented successfully. These technologies offer significant economic benefits, enable the production of a wider range of steel grades, and effectively handle sulfur and phosphorus. However, the growing demand for higher-quality steel and the expansion of the range of steel grades require further physical and chemical development of sponge alloys. This primarily concerns the production of iron-chromium sponge materials. Our research on the thermodynamic and kinetic characteristics of carbon-thermal and complex reduction of iron-chromium materials, including various man-made waste products with different chemical and mineralogical compositions, shows that such technologies are fundamentally feasible. In this regard, the metallurgy of special steel grades and powder metallurgy are both important areas of Fe-Cr alloy use. Based on the requirements for the quality of such materials, it is necessary to provide physical and chemical justification and to develop the main technological stages of the production process.

Purpose of the research

To investigate the solid-phase reduction process of chromium oxides at different temperatures and other influencing factors. To provide recommendations that ensure a high degree of chromium reduction with regulated carbon content.

The state of the issue

For the production of sponge ligatures, along with the solid-phase reduction of metal from its oxide [1, 2], the carbon content is of great importance and determines its market value and technological purpose. This indicator is regulated during the smelting of special grades of steel. Thermodynamically, solid-phase reduction of chromium oxides is possible with ultra-dry hydrogen ($H_2O < 0.05\%$) or with carbon. The formation of multiple carbides in the Cr-C system enables the reduction of Cr_2O_3 with solid carbon (or its monoxide) via various schemes. In this case, the reduction products may be stable or metastable solid phases. The conditions for the formation of these phases can be determined by thermodynamic analysis of the Cr-O-C system [3, 4]. However, the variety of reactions that occur during the reduction of Cr_2O_3 requires further research, specifically theoretical and experimental justification for obtaining ligatures with regulated carbon content.

Main results of the research

Figure 1 graphically represents the results of thermodynamic calculations of the Cr-O-C system performed using HSC [5] at a pressure of 1 (or 0.1) MPa for carbon-containing gases.

The three-component system under consideration has four degrees of freedom at a given pressure: C = k + 2 – f = 5 – 1 = 4. Variationless equilibrium occurs in the presence of four phases: reagents (Cr_2O_3 and C), one condensed product (Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$, or Cr), and the gas formed.

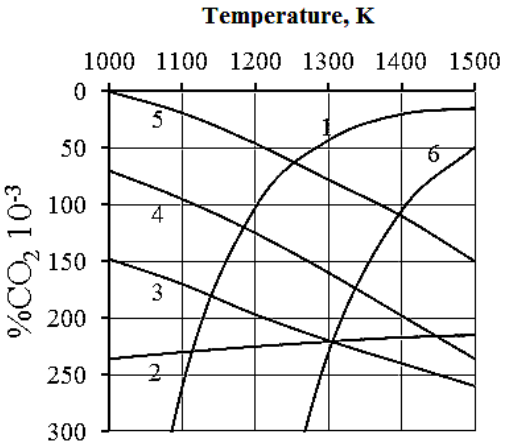


Figure 1 - Equilibrium diagram in the Cr-O-C system: 1 – $C + CO_2 = 2CO$;

2 – $\frac{1}{3}Cr_2O_3 + \frac{17}{9}CO = \frac{2}{9}Cr_3C_2 + \frac{13}{9}CO_2$;

3 – $\frac{1}{3}Cr_2O_3 + \frac{11}{7}CO = \frac{2}{21}Cr_7C_3 + \frac{9}{7}CO_2$;

4 – $\frac{1}{3}Cr_2O_3 + \frac{31}{23}CO = \frac{2}{69}Cr_{23}C_6 + \frac{27}{23}CO_2$;

5 – $\frac{1}{3}Cr_2O_3 + CO = \frac{2}{3}Cr + CO_2$;

6 – $\frac{7}{5}Cr_3O_2 + CO_2 = \frac{3}{5}Cr_7C_3 + 2CO$

Because the reduction of Cr_2O_3 with carbon has very low equilibrium CO_2 concentrations, the interactions in the system can be described by the following balance equations (1-5):

$$\frac{1}{3}Cr_2O_3 + \frac{13}{9}C = \frac{2}{9}Cr_3C_2 + CO, \quad (1)$$

$$\Delta G^0 = 237854 - 171{,}97 \cdot T;$$

$$\frac{1}{3}Cr_2O_3 + \frac{9}{7}C = \frac{2}{21}Cr_7C_3 + CO, \quad (2)$$

$$\Delta G^0 = 240802 - 171{,}59 \cdot T;$$

$$\tfrac{1}{3}Cr_2O_3 + \tfrac{27}{23}C = \tfrac{2}{69}Cr_{23}C_6 + CO, \quad (3)$$

$$\Delta G^0 = 246446 - 170{,}29 \cdot T;$$

$$\tfrac{1}{3}Cr_2O_3 + C = \tfrac{2}{3}Cr + CO, \quad (4)$$

$$\Delta G^0 = 255412 - 168{,}0 \cdot T;$$

$$C + CO_2 = 2CO, \quad (5)$$

$$\ln K_5 = -\frac{20035}{T} + 20{,}569$$

The lowest temperature corresponds to the temperature at which the recovery of Cr_2O_3 begins (T = 1383 K, reaction 1, Fig. 1). If there is excess carbon in the charge, all of the Cr_2O_3 will be consumed. The system will then remain in stable coexistence with C_{solid}, Cr_3C_2 carbide, and the gas phase, for which the ratio of CO_2 and CO in the entire temperature range under consideration must correspond to the equilibrium of reaction 1 (line 1 in Fig. 1).

In the case of a strictly stoichiometric ratio of the initial components in relation to reaction (1), both Cr_2O_3 and C_{solid} are consumed during the reduction process. At a fixed pressure, a system consisting of solid Cr_2O_3 reduction products and gases has two degrees of freedom. This allows the temperature and CO_2/CO ratio to be changed within the region bounded by lines 1, 2, and 6 (Fig. 1) without affecting the stability of the Cr_3C_2 carbide. Thus, analysis of the Cr-O-C system indicates that the specified temperature range corresponds to stable Cr_3C_2 carbide. A comparison of the Gibbs free energy change (ΔG^0) for reactions (1) - (4) per one gram-atom of reduced oxygen indicates a preference for Cr_2O_3 formation during Cr_7C_3 reduction under conditions of sufficient free carbon in the batch mixture. A change in thermodynamics occurs in the case of a carbon deficiency in the charge. At fixed values of P and T, the system reaches equilibrium only after the solid carbon phase (C_{solid}) disappears. However, as can be seen from Figure 1, chromium carbide (Cr_3C_2) stably coexists with excess Cr_2O_3 and gases up to ~1570 K (according to [1, 6], this occurs up to 1543 K or 1283 K, respectively). Above this temperature, in the presence of Cr_2O_3, the thermodynamics shift towards the formation of the intermediate carbide Cr_7C_3. The stability region of Cr_7C_3 (Figure 1) is bounded by lines 3 and 6. It can only coexist in equilibrium with excess chromium oxide or Cr_3C_2

carbides. The reduction of Cr_3C_2 by Cr_2O_3 occurs at temperatures above 1570 K, forming Cr_7C_3, and at temperatures above 1741 K, forming $Cr_{23}C_6$:

$$\frac{1}{3}Cr_2O_3 + \frac{9}{5}Cr_3C_2 = \frac{213}{15}Cr_7C_3 + CO, \quad (6)$$

$$\Delta G^0 = 264661,6 - 168,54 \cdot T;$$

$$\frac{1}{3}Cr_2O_3 + \frac{27}{28}Cr_3C_2 = \frac{13}{84}Cr_{23}C_6 + CO, \quad (7)$$

$$\Delta G^0 = 283757 - 163,008 \cdot T,$$

According to reaction (7), metastable $Cr_{23}C_6$ can appear at a temperature of ~1603 K, but only under conditions of high CO concentrations, which are supplied by reaction (8).

$$\frac{7}{5}Cr_2O_3 + CO_2 = \frac{3}{5}Cr_7C_3 + 2CO, \quad (8)$$

$$\ln K_8 = -\frac{22270}{T} + 20,283$$

With a limited amount of carbon in the charge, these patterns are confirmed by the temperature dependence of the Gibbs free energy for reactions (1) - (3). In this case, the C_{solid} is distributed between the reduction and carbide formation processes at the most favorable energy ratio (ΔG^0, J/K). This ratio is determined by the fact that forming chromium carbides is more favorable energetically than reducing Cr_2O_3: $\Delta G^0_{carb.} \le \Delta G^0_{red.}$ Under conditions of carbon deficiency, some Cr_2O_3 remains unreduced, and the corresponding reactions occur as follows:

$$\frac{3}{13}Cr_2O_3 + C = \frac{2}{13}Cr_3C_2 + \frac{9}{13}CO, \quad (9)$$

$$\Delta G^0 = 283757 - 163,008 \cdot T;$$

$$\frac{7}{27}Cr_2O_3 + C = \frac{2}{27}Cr_7C_3 + \frac{7}{9}CO, \quad (10)$$

$$\Delta G^0 = 283757 - 163,008 \cdot T;$$

$$\frac{23}{81}Cr_2O_3 + C = \frac{2}{81}Cr_{23}C_6 + \frac{23}{27}CO, \quad (11)$$

$$\Delta G^0 = 283757 - 163,008 \cdot T.$$

The existence of limits of thermodynamic stability for individual solid products of the carbon-thermal reduction of chromium oxide (Cr_3C_2 and Cr_7C_3) does not preclude the formation of other, less stable products. This

should be due to the successful development of reaction (5) (i.e., high concentrations of CO in the charge, as shown in Figure 1) and the slowed development of carbide formation reactions. If the reaction proceeds slowly, the formation of the intermediate carbide Cr_7C_3 is possible at temperatures below 1570 K.

$$\frac{3}{15}Cr_7C_3 + 2CO = \frac{7}{5}Cr_3C_2 + CO_2 \qquad (12)$$

These are the conditions under which the appearance of metastable trigonal carbide (Cr_7C_3) is possible. This is the development of the carbon gasification reaction (CO) and the slowing down of carbide formation reactions, i.e. certain thermodynamic and kinetic features that are formed in the system under study. Below 1297°C, the appearance of the intermediate carbide Cr_7C_3 is most likely under conditions of accelerated carbon gasification (reaction 1) and the slowed down course of reaction 8, which can be considered as accelerated gasification of Cr_3C_2 carbide with the formation of Cr_7C_3.

The formation of the unstable higher carbide Cr_3C_2 is possible at temperatures above 1570 K if reaction (8) is slow. At the same time, the need for a slow development of the associated reactions mentioned earlier (5, 8) remains. The formation of Cr_3C_2 in the reduction of chromium oxide is most likely when free carbon in the charge is consumed, and this contributes to the decarbonization of the reduction product. When we talk about decarburization, we mean obtaining a solid-phase reduction product with a lower carbon content. For example, when using Cr_3C_2 carbide in the reduction process of chromium oxide, we get a reduction in carbon from ~13% to 9%. Deeper decarburization (obtaining $Cr_{23}C_6$ carbide) is realized at temperatures above the solid-phase reduction temperatures, i.e. the appearance of liquid phases.

The thermodynamic prerequisites for developing the process in this way and reducing Cr_3C_2 using free carbon are significantly improved in the presence of metallic iron. The thermodynamic basis for developing a process in this way and reducing Cr_2O_3 with free carbon is significantly improved in the presence of metallic iron.

The authors [7] analyzed the Cr-Fe-O-C system for the formation of metal solutions containing 7% and 25% chromium. However, they did not consider the formation of mixed carbides $(Fe, Cr)_xC_y$. The established thermodynamic shifts revealed a substantial enhancement in the potential for carbon thermal reduction of Cr_2O_3 upon the incorporation of iron into the system. We obtained a similar result for processes involving C_{solid} and Cr_3C_2 with a wide range of Cr/Fe ratios in the resulting reduction product [8].

The authors [9, 10] carried out a detailed thermodynamic analysis of the Cr-Fe-O-C system (not related to the reduction process), taking into account the presence of metal solutions and carbide phases of different compositions [11]. In general, the results indicate that Cr_3C_2 carbide is unstable in the presence of iron. The mixed carbides $(Fe,Cr)_3C$, $(Cr,Fe)_7C_3$ and $(Cr, Fe)_{23}C_6$ coexist stably with the metal phase. The former form at low chromium concentrations, and the latter form at significant chromium concentrations. At the same time, carbide $(Fe,Cr)_7C_3$ has the widest scope of existence. The phase transformations that occur during the heat treatment of a Cr_3C_2 and iron mixture were studied experimentally in works [12, 13].

The analysis of the Cr-O-C and Cr-Fe-O-C systems indicates that the carbon content of the final product of solid-phase chromium reduction is significantly impacted by temperature, C/O and Cr/Fe ratios, and the addition of $Fe_{met.}$ However, it has been established that these parameters allow carbon to be reduced to ~2.0-2.5%. Experimental data indicate that the nature of the effect of $Fe_{met.}$ t additives on the kinetics of Cr_2O_3 reduction by free carbon and Cr_3C_2 carbide is directly opposite. The significant acceleration of the process in the latter case suggests additional methods for producing a solid product, such as diluting it with iron or increasing the involvement of the carbide phase in reducing chromium oxide. The kinetics of Cr_2O_3 reduction by the previously obtained Cr_3C_2 carbide alone and in the presence of an iron powder additive were studied. The carbide content of the charge provided a 50% reduction of the sample during the reaction (6). In the presence of iron additives at 1473 K, the reduction does not occur. Raising the temperature to 1573 K ensures that the process proceeds at a significant speed, and within 30 min. of the experiment, the degree of sample reduction approached the limit (46%). The transition to 1673 K greatly intensified the process, the degree of which (approximately 70%) significantly exceeded the previously indicated limit value of 50%. This indicates the formation of unstable $Cr_{23}C_6$ carbide, which becomes thermodynamically possible due to the accelerated reaction (8) and increased CO concentration in the charge volume due to the temperature increase to 1673 K (Fig. 1).

The introduction of metallic iron into the charge significantly changed the kinetic picture of the process. Notably, the presence of $Fe_{met.}$ ensures the reduction of Cr_2O_3 by Cr_3C_2 carbide at a temperature of 1473 K. Increasing the temperature to 1573 K accelerated the process, and introducing iron increased the speed by about 1.3 times. The degree of reduction of the sample in 0.5 hours was 70%. Similar shifts took place at 1673 K in the presence of iron, and the degree of reduction reached 80% within 20 minutes. The deep development of the process at 1573 and 1673 K

indicates the formation of a solid product based on lower chromium carbide ($Cr_{23}C_6$). This conclusion is consistent with the results of studies [12, 13].

The authors [12, 13], using various methods of physicochemical analysis, studied the phase transformations that occur during heat treatment of a pressed mixture of Cr_3C_2 and iron in a vacuum. They found that the interaction between the solid reagents begins with the diffusion of chromium and carbon atoms into metallic iron. The carbide is depleted of carbon, and its structure becomes looser. The carbide undergoes a redistribution of C atoms, and the orthorhombic structure of Cr_3C_2 is rebuilt into the hexagonal structure of Cr_7C_3. This hexagonal chromium carbide can dissolve up to 60% iron and transform into the common chromium-iron carbide $(Cr,Fe)_7C_3$. The migration of C and Cr from the initial Cr_3C_2 crystal lattice and their dissolution (substitution) in metallic iron can lead to the formation of complex carbides based on $Fe_{met.}$ According to authors [12, 13], further development of the process could lead to the formation of common carbides of the $(Cr, Fe)_{23}C_6$ type. This carbide was identified at 1373 K. The following probabilistic mechanism of the influence of $Fe_{met.}$ on the kinetics of carbon-thermal reduction of Cr_2O_3 can be formulated, taking into account the aforementioned information. As is known, higher chromium carbide replaces chromium atoms with iron atoms to a limited extent. The diffusion of carbon atoms into metallic iron is difficult because the iron is already heavily carburized as a result of the reactions:

$$2CO = CO_2 + [C]_{Fe}, \tag{13}$$

$$2CO + 3Fe = Fe_3C + CO_2, \tag{14}$$

$$\ln K_{14} = -\frac{18798.6}{T} + 19,3457$$

The migration of Cr atoms from carbide to $Fe_{met.}$ cannot develop without the accompaniment (or advanced diffusion) of carbon. Therefore, the formation of solid solutions of Fe-Cr-C and common carbides $(Fe,Cr)_3C$ is greatly limited in the presence of free carbon, especially at relatively low temperatures. The influence of iron additives in the charge is mainly limited to the aforementioned directions.

The consumption of C_{solid} and the involvement of Cr_3C_2 in the Cr_2O_3 reduction process radically changes the situation. Due to the development of reaction (8), a carbon deficiency occurs on the carbide surface, resulting in the phase transformation of Cr_3C_2 to Cr_7C_3. Without free carbon, reactions (13) and (14) are complicated, and their reverse direction are possible. This opens paths for the counter-diffusion of Cr and Fe atoms, resulting in the

formation of iron-chromium carbide $(Cr,Fe)_7C_3$ and Fe-Cr-C solutions. The formation of the carbide $(Fe,Cr)_3C$ is less likely under the conditions of reaction (8). This is supported by the significantly greater strength of Cr_3C_2 compared to Fe_3C – the decrease in free energy during formation of the latter is much smaller than the similar value for higher chromium carbide. The presence of up to 20% chromium (Cr) in the iron (Fe) crystal lattice [14] cannot reverse the ΔG^0 ratio. At the same time, the process further develops to produce mixed carbide $(Cr, Fe)_{23}C_6$ [12, 13].

The formation of Fe-Cr-C solutions and mixed carbides results in significant thermodynamic shifts within the system under consideration. Specifically, the decrease in chromium activity resulting from its dissolution in iron, coupled with the increase in equilibrium CO_2 concentrations, creates favorable conditions for the development of reaction (15) [7-9].

$$\frac{1}{3}Cr_2O_3 + CO = \frac{2}{3}Cr + CO_2, \qquad (15)$$

$$\ln K_{15} = -\frac{10716,3}{T} - 0,335.$$

However, this link does not determine the rate of the observed process. The studies conducted in this work demonstrate that reaction (5) plays a primary role in determining the rate. This is evidenced by the increased rate of Cr_2O_3 reduction when carbon is ground, its content in the charge increases, and graphite is replaced by highly reactive charcoal or pyrolignin.

Introducing Cr_3C_2 into the reduction of Cr_2O_3 changes the nature of the interaction by forming the mixed carbide $(Cr,Fe)_7C_3$. This mixed carbide can be considered a practically ideal chromium-iron solution in the substitution sublattice of the common carbide [15, 16]. The formation of such a solution promotes the development of reactions (16) and (8) due to a decrease in the activity of the carbide phase.

$$\frac{1}{3}Cr_2O_3 + \frac{11}{7}CO = \frac{2}{21}Cr_7C_3 + \frac{9}{7}CO_2, \qquad (16)$$

$$\ln K_{16} = -\frac{3232,9}{T} - 5,786.$$

Therefore, reaction (6), which describes the general reduction of Cr_2O_3, is accelerated with the replacement of Cr_7C_3 by $(Cr, Fe)_7C_3$.

The influence of Fe_{met} on the kinetics of Cr_2O_3 reduction by carbon varies depending on the stage of the process. Under conditions of a significant shortage of C_{solid}, the transition from inhibition to intensification of the process is clearly evident. Furthermore, as previously mentioned, the extent of process development surpasses the $Cr_2O_3 \rightarrow Cr_7C_3$ transition

process, indicating the formation of an iron-chromium carbide phase based on $Cr_{23}C_6$. Metal atom diffusion is not one-way. Therefore, due to chromium diffusing into metallic iron, an Fe-Cr-C solution forms. Similar processes develop when the previously obtained Cr_3C_2 carbide reduces Cr_2O_3.

The results of the studies performed indicate the possibility of quickly reducing Cr_2O_3 completely in the presence of iron, for example, at 1673 K. The metallized product obtained under these conditions undergoes significant decarburization. Calculations show that, with a Cr_2O_3-to-C_{solid} ratio in the charge corresponding to reaction (2) and an atomic ratio of Cr/Fe ≈ 1, the carbon content in the final product is ~4.5%. The charge mixture corresponding to reaction (3) reduces the carbon concentration to ~2.5%.

Replacing $Fe_{met.}$ with iron oxides does not affect the speed of the process. This is evidenced by the results of jointly reducing iron and chromium from a mixture of magnetite and chromium concentrates at 1673 K. However, it should be noted that replacing Cr_2O_3 with a natural material significantly decreases the reduction rate, according to the results of the studies.

Optimization of the parameters of the solid-phase reduction of chromium process: T, C/O, Cr/Fe, Fe/Ni, reduction time and hydrogen fraction in the gas phase, ensures the production of iron-chromium alloy with a carbon content of 2.0 - 2.5%. Regression equations describing the content of bound (C_b) and total (C_Σ) carbon in the alloy as a function of the specified process parameters were obtained [2]:

$$\%C_b = 4,701 + 1,430 \cdot X_1 + 1,54 \cdot X_2 - 1,479 \cdot X_3 - 0,547 \cdot X_4 - 0,582 \cdot X_5 - 0,008 \cdot X_6 \quad (17)$$

$$\%C_\Sigma = 16,025 - 0,165 \cdot X_1 - 2,645 \cdot X_2 - 0,945 \cdot X_3 + 1,037 \cdot X_4 + 0,735 \cdot X_5 + 0,228 \cdot X_6 \quad (18)$$

where X_1 – time, min.; X_2 – temperature, K; X_3 – Cr/Fe; X_4 – Fe/Ni, X_5 – O/C and X_6 – H_2. The correlation coefficient is 0.894 and 0.901, respectively, for (17) and (18).

The analysis of the obtained results allows us to draw the following preliminary conclusions:

1. Selecting conditions for reducing a complex charge enables the production of a multicomponent alloy with a low carbon content.

2. Increasing the process temperature, reduction time, and O/C ratio most affects the increase in carbon.

3. Decreasing the carbon content in the alloy is achieved by reducing the Cr/Fe ratio and increasing the Fe/Ni ratio and the O/C ratio.

4. Introducing hydrogen into the system at a constant O/C ratio also affects the carbon content of the alloy, albeit to a lesser extent.

However, the resulting carbon content does not meet the requirements for an alloy used to smelt special steel grades. Further reducing the carbon content is possible through additional processing of the sponge alloy.

Based on the physicochemical analysis data of the process for producing a product with low C_{solid} content, as well as data [16], it is possible to propose options for reducing the carbon content of the resulting spongy ligature, such as oxidative decarburization by gas phase or by bound oxygen.

In the temperature range that prevents melting of the charge, carbon-thermal reduction and complex reduction of chromium (III) oxide occur in the following stages: $Cr_2O_3 \rightarrow Cr_3C_2$ and $Cr_2O_3 \rightarrow Cr_7C_3$ [17-19]. Further development of the process requires increasing the temperature to 1828 K or higher. This is evidenced by calculations based on the set of reactions.

$$\frac{1}{3}Cr_2O_3 + CO + \frac{4}{27}Cr_7C_3 = \frac{2}{27}Cr_{23}C_6 + CO_2, \quad (19)$$

$$\frac{23}{27}Cr_7O_3 + CO_2 = \frac{7}{27}Cr_{23}C_6 + 2CO, \quad (20)$$

$$\frac{1}{6}Cr_{23}O_6 + CO_2 = \frac{23}{6}Cr + 2CO. \quad (21)$$

The calculated equations were obtained by transforming the equilibrium constant expressions of the above reactions according to the earlier implemented algorithm highlighted in [20]. For the first stage of the process ($Cr_7C_3 \rightarrow Cr_{23}C_6$), the following equation was obtained:

$$\alpha = K_{19} \cdot K_{20} \cdot (1 + K_5). \quad (22)$$

At the second stage ($Cr_{23}C_6 \rightarrow Cr$) the following equation is valid:

$$\alpha = K_{15} \cdot K_{21} \cdot (1 + K_{16}). \quad (23)$$

Where $\alpha = P_{CO} + P_{CO_2}$ in relative units; K_{15} and K_{16} are the equilibrium constants of the reduction reactions $Cr_2O_3 \rightarrow Cr_7C_3$ and $Cr_2O_3 \rightarrow Cr_{23}C_6$, respectively; K_{11} and K_{17} are the equilibrium constants of the gasification reactions of carbides.

Table 1 shows the calculation of the thermodynamically permissible temperatures for the reduction of Cr_2O_3 to $Cr_{23}C_6$ and metallic chromium.

Table 1 – Thermodynamically permissible temperatures for the onset of reduction of Cr_2O_3 to $Cr_{23}C_6$ and metallic chromium

α	β	Temperature of process stage, K	
		$Cr_7C_3 \rightarrow Cr_{23}C_6$	$Cr_{23}C_6 \rightarrow Cr$
0,75	0,25	1934,38	1975,36
0,5	0,5	1894,65	1933,91
0,25	0,75	1828,65	1866,87

Due to the unacceptably high temperatures of the process stages, a method of oxidatively treating the obtained ligature was proposed. A thermodynamic analysis was performed to study the possibility of oxidative decarburization of the carbide phase at the $Cr_7C_3 \rightarrow Cr_{23}C_6$ stage based on reaction (20) and the following reaction:

$$H_2O + CO = H_2 + CO_2. \qquad (24)$$

Reduction reactions provide the transformation $Cr_7C_3 + H_2O \rightarrow Cr_{23}C_6 + H_2$. To calculate equilibrium quantities P_{H_2O} and P_{H_2} it is necessary first to determine the equilibrium pressure of carbon-containing gases at a given level α:

$$K_{16} = \frac{P_{CO}^2}{P_{CO_2}} = \frac{X^2}{\alpha - X}, \text{ where } X^2 + K_{16} \cdot X - K_{16} \cdot \alpha = 0.$$

Using the found values $P_{CO} = X$, $P_{CO_2} = \alpha - X$ we transform the equilibrium constant of link (20):

$$K_{20} = \frac{P_{H_2} \cdot P_{CO_2}}{P_{H_2O} \cdot P_{CO}}; \qquad P_{H_2} \Big/ P_{H_2O} = K_{20} \cdot P_{CO} \Big/ P_{CO_2} = A$$

Denoting $P_{H_2} + P_{H_2O}$ by β and taking into account that β = 1 – α, we make the following transformations:

$$P_{H_2} \Big/ P_{H_2O} = \frac{\beta - P_{H_2O}}{P_{H_2O}} = A \quad \text{and} \quad P_{H_2O} = \frac{\beta}{(1 + A)}.$$

The methods for solving the obtained equations are provided in [18]. Figure 2 illustrates the equilibrium composition of the gas phase at different temperatures and α/β ratios.

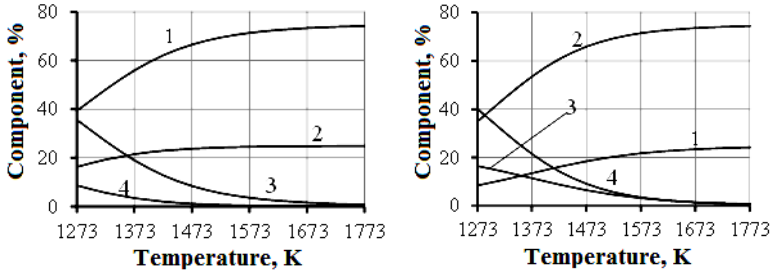


Figure 2 – Equilibrium gas composition of the first stage of oxidative decarburization ($Cr_7C_3 \rightarrow Cr_{23}C_6$): a) – α = 0,25, β = 0,75; b) – α = 0,75, β = 0,25;1 – H_2; 2 – CO; 3 – H_2O; 4 – CO_2

The thermodynamic feasibility of oxidatively decarburizing $Cr_{23}C_6$ carbide, producing metallic chromium, can be estimated using the reaction systems (17) and (20). Through transformations similar to those performed above, we derive the following equation:

$$X^2 + K_{17} \cdot X - K_{17 \cdot \alpha} = 0 \quad \text{and} \quad P_{H_2O} = \frac{\beta}{(1+A)}.$$

where the value of A is determined taking into account the level of P_{CO} and P_{CO_2} corresponding to the equilibrium of link (17). The calculated data of the equilibrium composition of the gas phase at different temperatures and α/β ratios are illustrated in Figure 3.

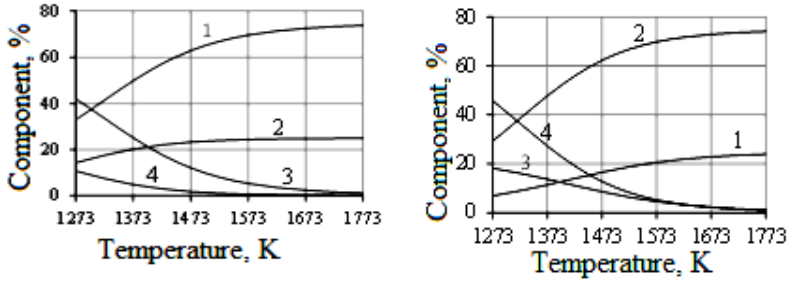


Figure 3 – Equilibrium composition of the gas phase in the second stage of oxidative decarburization ($Cr_{23}C_6 \rightarrow Cr$): a) – α = 0,25,β = 0,75; b) – α = 0,75,β = 0,25, 1 – H_2; 2 – CO; 3 – H_2O; 4 – CO_2

The results of the analysis indicate the presence of thermodynamic prerequisites for the organization of oxidative decarburization of chromium carbides at moderate temperatures of up to 1623 K. Oxidative decarburization at the $Cr_7C_3 \rightarrow Cr_{23}C_6$ stage is possible and can be implemented in an H_2-H_2O flow.

Another option for organizing the oxidative decarburization of chromium carbides in an Ar – H_2O flow is also worth noting. In this case, the concentration of water vapor must exceed that in the mixture P_{H_2O} and P_{H_2} at a given temperature and value of β.

The spongy ligature can be refined using bound oxygen. The carbon ligature obtained in the first stage can then be used as a reducing agent for oxides such as NiO, Fe_3O_4, etc. Physicochemical justification of this process requires an assessment of the thermodynamic possibility of reducing the components of a complex charge with carbon carbide within the temperature limits of solid-phase reduction. Transformation of the carbide phase and change in composition and morphology require an assessment of its reducing ability in relation to the components of the charge, taking into account process conditions. Criteria for this assessment include the temperature of the onset of carbide gasification (steam), the temperature of the onset of oxide reduction by carbide, and the equilibrium composition of the gas phase of the MeO(1)-MeO(2)-MeS system.

Figure 4 shows the calculated composition of the equilibrium gas phase during carbidothermic (Cr_7C_3 and $Cr_{23}C_6$) reduction of some oxides.

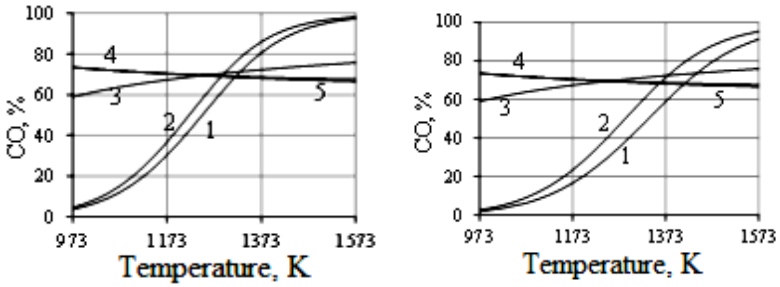


Figure 4 – Equilibrium composition of the gas phase of carbidothermal reduction of oxides: a) α = 0,25, b) α = 0,75; 1,2 – gasification $Cr_{23}C_6$ and Cr_7C_3; 3 – FeO; 4 – WO_2; 5 – MoO_2

Data analysis shows that reducing the specified oxides with chromium carbides is thermodynamically possible. However, oxides such as MnO and VO cannot be reduced by chromium carbides within the specified temperature range.

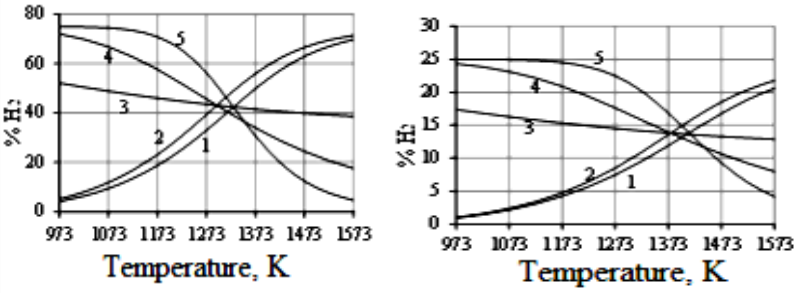
In this case, manganese and vanadium can be introduced into the ligature using their carbides, MnC_2 and VC, which are formed during the carbon thermal reduction of the corresponding metal oxides. Alternatively, they can be introduced as a component of technogenic waste. The introduced carbides are gasified by CO_2, H_2O or bound oxygen, providing a reduction potential of the gas phase and promoting the reduction of other oxides.

A similar method was used to perform thermodynamic analysis of the complex reduction of various oxygen-containing compounds with the participation of carbides, which allows us to assess the possibility of reduction in a temperature range that excludes the formation of liquid phases. Using a similar method as for NiO, we calculated the equilibrium composition of the gas phase of carbon thermal and complex reduction for some oxides with respect to different C/O and C/H ratios.

Figures 5 and 6 show the calculated gas phase compositions of the complex reduction of FeO, MoO, and MoO_2.

$$\frac{96}{138}MoO_2 + H_2 + \frac{1}{3}Cr_7C_3 = \frac{96}{138}Mo + \frac{27}{69}CO + \quad (25)$$
$$+H_2O + \frac{7}{69}Cr_{23}C_6$$

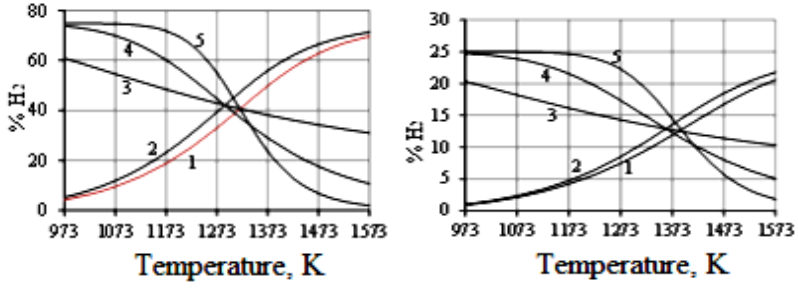
$$MoO_2 + H_2O + \frac{1}{6}Cr_{23}C_6 = Mo + CO + H_2O + \frac{23}{6}Cr. \quad (26)$$



(a) (b)

Figure 5 – Equilibrium composition of the gas phase during the complex reduction of FeO by carbides at: a) α = 0,25; β = 0,75; b) α = 0,75; β = 0,25; 1,2 – gasification of carbides $Cr_{23}C_6$ and Cr_7C_3, respectively; 3 – reduction by H_2; 4,5 – reduction of (H_2+ Cr_7C_3) and (H_2+ $Cr_{23}C_6$)

The research results showed that it is possible to decarburize the complex spongy alloy to a level corresponding to the carbon content dissolved in chromium. Further oxidation treatment may result in the oxidation of the alloying element. Additionally, it is important to note that breaking down the carbide phase should be done in stages to avoid the transition $Cr_{saturated\ C} \rightarrow Cr$.



(a) (b)

Figure 6 – Equilibrium composition of the gas phase during the complex reduction of MoO2 by carbides at: a) α = 0,25; β = 0,75; b) α = 0,75; β = 0,25; 1,2 – gasification of carbides $Cr_{23}C_6$ and Cr_7C_3, respectively; 3 – oxide reduction by hydrogen; 4,5 – reduction according to reactions (25) and (26).

Conclusions

1. The technology of solid-phase reduction of chromium and iron oxides can be used with substandard ores and waste as charge components to produce spongy alloys at low energy costs. The resulting product can be used not only in the smelting of special steel grades, but also as a component for powder metallurgy.

2. A comprehensive physicochemical justification of reducing the carbon content in products of solid-phase joint reduction of chromium and iron has been conducted. The results of the presented analysis indicate that the carbon content can be reduced to 2.0-2.5% under the appropriate process organization conditions.

3. It has been established that further decarburization is possible through additional thermochemical treatment of the reduction product. Scientifically substantiated and experimentally confirmed that carbon reduction can be achieved by treating a spongy ligature with a gas mixture of H_2 – H_2O (Ar – H_2O) at a temperature of 1273–1373 K and a H_2O concentration of 1–2% for 25–40 minutes.

4. Carbon reduction is also possible with the involvement of bound oxygen. The carbide phase obtained in the first stage of the complex reduction of the oxide charge is used in the subsequent joint reduction of chromium ore and magnetite concentrate.

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ТЕОРЕТИЧНЕ ТА ЕКСПЕРИМЕНТАЛЬНЕ ОБҐРУНТУВАННЯ ТВЕРДОФАЗНОГО ВІДНОВЛЕННЯ ХРОМУ ТА ЗАЛІЗА З ЇХ ОКСИДІВ

Анотація. Отримання якісних марок сталі, в умовах підвищення дефіциту мінеральних та енергетичних ресурсів, ставить перед металургією найважливіше завдання, зокрема вдосконалення існуючих та розробка нових технологій виробництва легуючих матеріалів з використанням некондиційних руд та відходів. Одним з перспективних технологічних напрямків є технологія твердофазного відновлення (ТВ), яка забезпечує отримання з комплексної шихти губчастих лігатур при температурах, нижчих від температури плавлення шихти, що сприяє зниженню енергетичних витрат, а також забезпечує зменшення вмісту в металі шкідливих елементів, зокрема сірки, та за певних умов фосфору. Технологічні особливості ТВ вигідно відрізняють цей процес від традиційного феросплавного виробництва. Використаний в даній роботі підхід до термодинамічного дослідження системи Cr-O-C відображає провідний напрямок механізму твердофазного відновлення оксиду хрому вуглецем. При цьому процес розвивається головним чином через парогазову фазу з визначальною роллю газової фази (CO-CO_2), що здійснює зв'язок між твердими реагентами. Встановлено, що подальше зневуглецювання в продуктах твердофазного спільного відновлення хрому та заліза можливо шляхом додаткової термохімічної обробки продукту відновлення. Науково обґрунтовано та експериментально підтверджено зменшення вуглецю шляхом обробки губчастої лігатури газовою сумішшю H_2 – H_2O або Ar – H_2O при температурі 1273 – 1373 К і концентрації H_2O на рівні 1 - 2%, протягом 25 - 40 хв.

Ключові слова: твердофазне відновлення, вуглецевотермічне відновлення, карбідоутворення, оксид хрому, карбід хрому, фізико-хімічні властивості, енергія Гіббса.

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