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THERMODYNAMIC REGULARITIES OF OBTAINING SPONGY LIGATURES WITH LOW CARBON CONTENT

A thermodynamic analysis was carried out on the subject of metal oxides and ferrites reduction both with chromium carbide Cr_7C_3 individually and in combination with a hydrogen stream to obtain low-carbon chromium-based ligatures. It was shown the possibility of organizing such a process in the temperature range excluding charge melting. The obtained data confirmed that the proposed method can produce sponge ligatures based on chromium of complex composition.

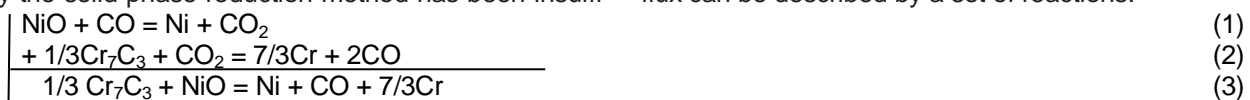
Keywords: chromium carbide, sponge ligature, thermodynamic analysis, carbon-thermal and complex reduction, oxide, ferrite.

Виконано термодинамічний аналіз процесів відновлення оксидів металів і феритів карбідом хрому Cr_7C_3 самостійно і в комбінації з потоком водню стосовно отримання лігатури на основі хрому з низьким вмістом вуглецю. Показана можливість організації такого процесу в області температур, що виключають плавлення шихти. Отримані дані дозволяють зробити висновок, що запропонованим способом можна отримати губчасті лігатури на основі хрому комплексного складу.

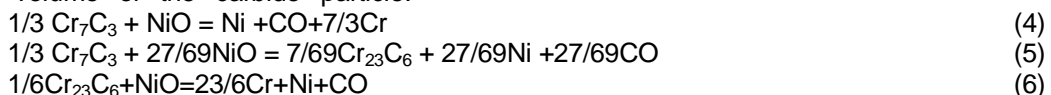
Ключові слова: карбід хрому, губчаста лігатура, термодинамічний аналіз, вуглецево-термічне та комплексне відновлення, оксид, ферит.

Sponge and powder ligatures have a unique complex of technological properties, which makes it possible to use them for special steel grades and alloys smelting, as well as in powder metallurgy. The use of spongy and powder ligatures can significantly reduce the cost of basic and auxiliary materials, energy resources and to extract alloying elements from ores to a greater extent.

The use of complex sponge ligatures also makes it possible to significantly increase operating properties of the products obtained [1, 2]. However, up to the present time, the problem of obtaining of complex composition sponge ligatures with low carbon content by the solid-phase reduction method has been insuffi-



The link of carbide gasification, in accordance with the principle of the sequence of transformations, is realized as: $Cr_7C_3 \rightarrow Cr_{23}C_6 \rightarrow Cr_{sat-d} C$. The physico-chemical model of Cr_7C_3 gasification can be carried out in a stepwise or zonal scheme depending on the diffusion and chemical parameters. Under the conditions providing the zonal gasification regime, the following transformations take place simultaneously: $Cr_7C_3 \rightarrow Cr_{23}C_6$ and $Cr_{23}C_6 \rightarrow Cr$, which are spatially separated in the volume of the carbide particle.



As can be seen in Figure 1, at temperatures above ~ 1073 K, the gasification process is thermodynamically more preferable for reactions 4 and 6. Proceeding from this, the gasification of the carbide Cr_7C_3 was further examined by reaction 4.

Thermodynamic parameters that determine the possibility of reducing the oxide (or more complex compound) at a constant pressure are the temperature and composition of the gas phase. The presented

ciently studied. In some publications [1, 3] the authors propose a solution with a limited O/C ratio, which significantly narrows the composition of ligatures.

The aim of this work is the development of thermodynamic bases for obtaining a complex ligature by the solid-phase reduction of oxides with the participation of chromium carbide. The proposed method for obtaining the master alloy consists of the complex reduction of oxides mixture by the previously obtained chromium carbide Cr_7C_3 . Initially, the possibility of such a process was analyzed for the reduction of nickel oxide by trigonal chromium carbide. A purely carbothermic as well as complex reduction in the CO flux can be described by a set of reactions:

Indirect confirmation of the zonal flow of the process is obtained by the composition of the gaseous phase, formed at the stage of $(Cr_7C_3 \rightarrow Cr_{23}C_6) + NiO$. A high concentration of CO_2 initiates simultaneously the second stage of gasification of $Cr_{23}C_6 \rightarrow Cr$ and further reduction of nickel oxide. Possible variants of carbide participation during the reduction of nickel oxide are represented by the reactions:

system (reactions 1 - 3) is formed by four components (K) and contains five phases (F). It has, according to the rule of phases: $V = K + 2 - F$, one degree of freedom (V - variance). At a fixed pressure of carbon-containing gases ($P_{CO} + P_{CO_2} = \alpha$), equilibrium occurs under conditions of a single, completely defined temperature (T_{eq}). It can be determined on the basis of the equilibrium constants of the reactions (1) and (2). The latter can be represented in the form:

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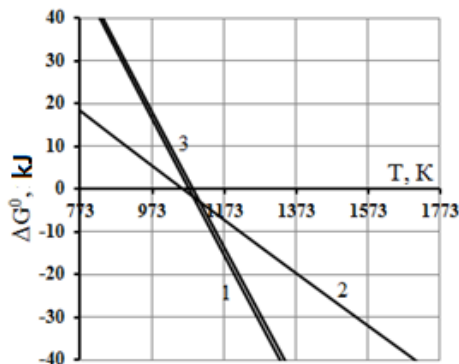


Fig. 1. Temperature dependence of free energy change (ΔG^0) in reactions:

1. $1/3 Cr_7C_3 + NiO = Ni + CO + 7/3Cr$;
2. $1/3Cr_7C_3 + 27/69NiO = 7/69Cr_{23}C_6 + 27/69Ni + 27/69CO$;
3. $1/6Cr_{23}C_6 + NiO = 23/6Cr + Ni + CO$.

$$K_2 = \frac{P_{CO}^2}{P_{CO_2}} = \frac{P_{CO}}{K_1}, \text{ since } K_1 = \frac{P_{CO_2}}{P_{CO}}. \text{ So, } P_{CO} = K_1 \cdot K_2$$

Representing the equilibrium constant of the link (1) in the form $K_1 = \frac{\alpha - P_{CO}}{P_{CO}}$,

we obtain the ratio
$$P_{CO} = \frac{\alpha}{(1 + K_1)}$$

$$\alpha = \exp\left(a_0 + \frac{a_1}{T}\right) \cdot \exp\left(B_0 + \frac{B_1}{T}\right) \cdot \left[1 + \exp\left(a_0 + \frac{a_1}{T}\right)\right], \tag{8}$$

For some oxides, the start temperature of reduction was calculated for different values of α . The results are shown in Table 1.

The equilibrium composition of the gas phase also determines the thermodynamics of the process. The equations, obtained earlier, allow us to determine the composition of the gas phase in the reaction (1) at temperatures $T \leq T_{eq}$:

$$P_{CO} = \alpha / (1 + K_1) \text{ and } P_{CO_2} = \alpha - P_{CO}.$$

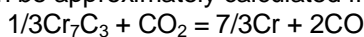
For the zonal or stepwise mode of the gasification process, the composition of the gas phase will be dif-

ferent, which will affect the thermodynamics of the nickel oxide reduction by Cr_7C_3 carbide. The composition of the gas phase in the zonal gasification regime can be approximately calculated from the reaction:

$$\alpha = K_1 \cdot K_2 \cdot (1 + K_1) \tag{7}$$

The equation presented earlier [4,5] allows to determine the value of T_{eq} for various values of α :

ferent, which will affect the thermodynamics of the nickel oxide reduction by Cr_7C_3 carbide. The composition of the gas phase in the zonal gasification regime can be approximately calculated from the reaction:



$$K_2 = \frac{P_{CO}^2}{P_{CO_2}} = \frac{X^2}{\alpha - X}, \text{ hence } X^2 + K_2 \cdot X - K_2 \cdot \alpha = 0$$

, where $\alpha = P_{CO} + P_{CO_2}$

The data obtained on the composition of the gas phase for the Ni-Cr-O-C system are shown in Fig. 2.

Table 1 - Start temperatures of oxide reduction

α	0,15	0,25	0,35	0,45	0,55	0,65	0,75	0,85	0,95	1,0
NiO	727.8	745.5	757.8	767.2	774.8	781.3	786.9	792.0	796.5	798.6
Fe ₂ O ₃	459.9	466.5	470.9	474.3	477.1	479.4	481.4	483.1	484.7	485.4
Fe ₃ O ₄	1184.9	1209.9	1227.2	1240.2	1250.8	1259.9	1267.6	1274.5	1280.7	1283.5
FeO	1277.1	1313.2	1338.1	1357.2	1372.8	1386.2	1397.8	1417.4	1417.4	1421.7
MoO ₂	1273.6	1304.1	1324.9	1340.7	1353.8	1364.8	1374.5	1383.0	1390.7	1394.0
WO ₃	1055.2	1085.5	1106.4	1122.6	1135.9	1147.2	1156.9	1165.7	1173.5	1177.1
WO ₂	1273.6	1304.1	1324.9	1340.7	1353.8	1364.8	1374.5	1383.0	1390.7	1394.2
Fe ₂ MnO ₄	1413.8	1449.3	1473.7	1492.6	1507.9	1520.9	1532.3	1542.4	1551.4	1555.6

According to the proposed method, the equilibrium composition of the gas phase is calculated for the reduction of iron oxides by Cr_7C_3 carbide, the results are shown in Fig. 3. The reduction proceeds successively $Fe_3O_4 \rightarrow FeO \rightarrow Fe$, but the process regime is more likely to be stepwise, however, this requires additional analysis.

Table 1 presents the results of calculating T_{eq} of iron oxides reduction with chromium carbide, which correlate with figure 3. The sequence and mechanism of solid product formation in this process are insufficiently investigated.

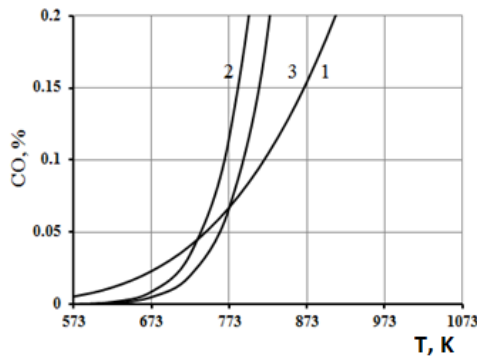


Fig. 2. Equilibrium in the Ni-Cr-C-O system

- 1. NiO + CO = Ni + CO₂
- 2.3. 1/3 Cr₇C₃ + CO₂ = 7/3 Cr + 2CO
at α = 0.25 and 0.75, respectively

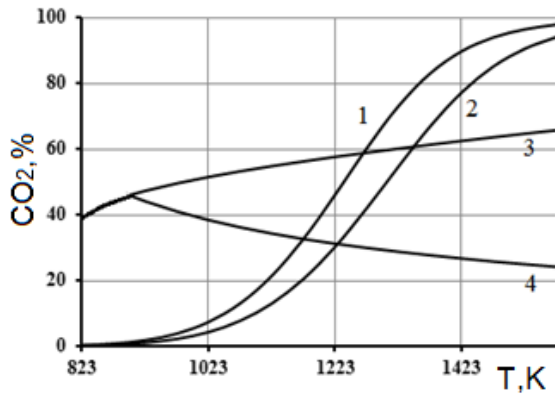


Fig.3. Equilibrium in Fe – Cr – C – O system:
1, 2 – 1/3Cr₇C₃ + CO₂ = 7/3Cr + 2CO,
if α = 0,25 and 0,75;
3 – FeO + CO = Fe + CO₂;
4 – Fe₃O₄ + CO = 3FeO + CO₂.

Along with the metal oxides, other oxygen-containing compounds may also participate in the reduction process, for example, the components of the rolling mill scale - ferrites: NiFe₂O₄, CoFe₂O₄,

Fe₂MnO₄, etc. Thermodynamic analysis has shown the possibility of their reduction by chromium carbides under given temperature conditions. The results are presented in Fig. 4.

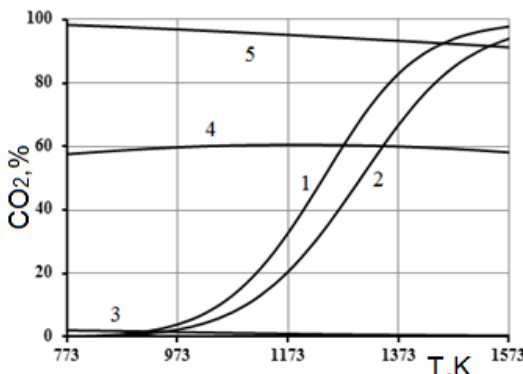


Fig.4. Carbon-thermal reduction of ferrites by Cr₇C₃:
1, 2 – gasification of carbide with CO₂ at α = 0.25 and 0.75 respectively;
3 – NiFe₂O₄; 4 – CoFe₂O₄; 5 – Fe₂MnO₄.

However, some difficultly reducible oxides under the given temperature conditions cannot be thermodynamically reduced with chromium carbides. The introduction of such metals into the ligature is possible with their carbides, which also will increase the reduction capacity of the system.

The participation of the carbide phase in the process of carbothermic or complex reduction is realized through the gasification unit [6]. The possibility of using the reduction potential of carbides (introduced or formed) at given temperature limits can be estimated from the temperature of their gasification beginning. For a number of carbides, the obtained values of the gasification start temperature are shown in Table 2.

The results show that all this carbides, except Mn₇C₃ and MnC₂, gasify at a given temperature range. To come over the thermodynamic prohibition, emerging for individual carbides, is possible with use of a stronger oxidizer - oxygen, or by the introduction of

this metal into the initial charge in other chemical form. The real picture of the carbide phase formation and participation in the process of carbothermic reduction of oxides is much more complicated due to the formation of complex carbides of variable composition, for example M₇C₃, where M is Cr, Fe, Ni. To assess the physicochemical patterns of their participation in the reduction process is possible with thermodynamic modeling methods using special programs (for example – Fact Sage). Introduction of hydrogen to the system, i.e. transition to a complex reduction involving chromium carbides, significantly changes the thermodynamic picture of the process. In parallel with reactions 1, 2, the following reactions are triggered:

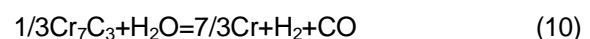


Table 2- The start temperatures of carbides gasification

Element	Carbide	T, K at $\Delta G^{\circ} = 0$	
		CO ₂	H ₂ O
Fe	Fe ₃ C	958.885	926.532
Cr	Cr ₃ C ₂	1093.57	1093.17
	Cr ₇ C ₃	1352.24	1413.26
	Cr ₂₃ C ₆	1384.68	1454.67
Ni	Ni ₃ C	634.171	521.616
Mn	Mn ₇ C ₃	1587.96	1682.09
	Mn ₃ C	-	-
	Mn ₁₅ C ₄	-	-
	Mn ₂₃ C ₆	1228.42	1252.19
Mo	MoC	1042.12	1030.4
	Mo ₃ C ₂	805.531	727.224
	Mo ₂ C	1329.61	1378.23
W	WC	1227.16	1248.23
	W ₂ C	1119.34	1125.3
V	VC	1418.73	1485.22
	V ₂ C	1513.45	1595.17

The latter, together with the reaction (2), makes it possible to describe adequately the unit of steam gasification of Cr₇C₃. The peculiarity of this link is characterized by the fact that the formation of hydrogen is accompanied by the appearance of a mixture of CO-CO₂, the ratio of which is determined by the temperature and the proportion of carbon- and hydrogen-containing gases in the reaction mixture. Reaction

9 can be replaced by reactions 3 and 11. The temperature of the complex reduction beginning corresponds to the onset of steam gasification of the carbide. Calculation of the equilibrium composition of the gas phase was carried out according to the procedure described earlier [7]. Figure 5 shows the results of calculating the equilibrium in the Cr-Ni-C-H-O system.

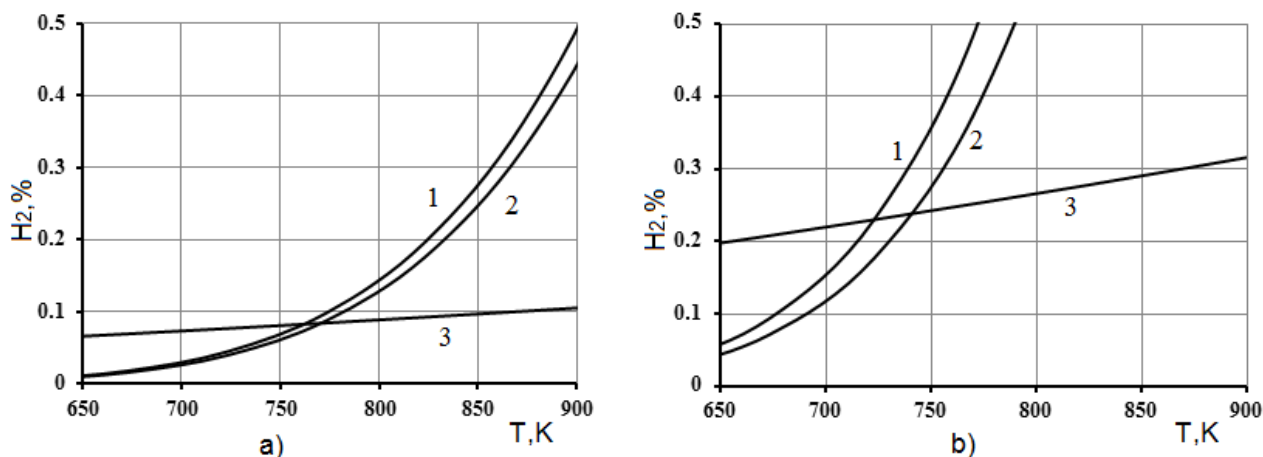


Fig.5. Equilibrium in Cr – Ni – O – C – H system at: a) $\alpha=0.75, \beta=0.25$; b) $\alpha=0.25; \beta=0.75$

Hydrogen positively influences on the thermodynamic conditions of the process, reducing the temperature. Simultaneously, partial replacement of carbon in carbide phase by hydrogen promotes the decarburization of the product, and also allows expanding the composition of the initial charge. The water vapor formed in this case thermodynamically favors the gasification of carbide [8], being a stronger oxidant. However, a detailed physical-chemical analysis is needed to determine the contribution of hydrogen and carbide

carbon in the reduction process in order to minimize the residual carbon in the system.

All the above thermodynamic features are also retained in the complex reduction of ferrites. Figure 6 shows the temperature dependence of the equilibrium composition of the gas phase of the complex reduction of Fe₂MnO₄. Increasing the proportion of hydrogen significantly reduces the start temperature of reduction.

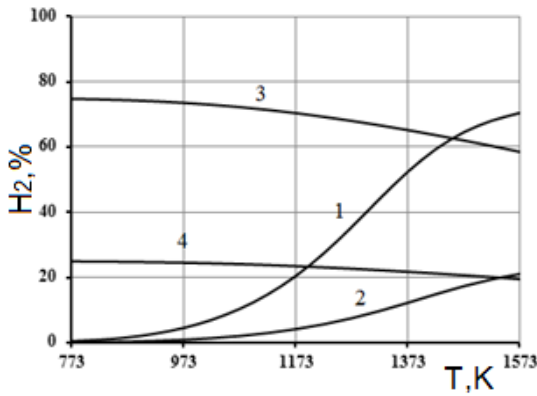


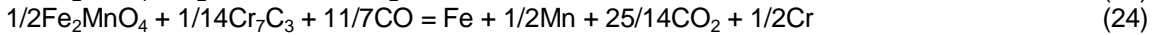
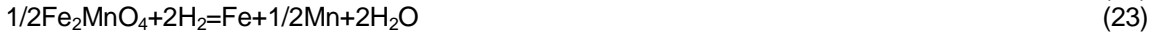
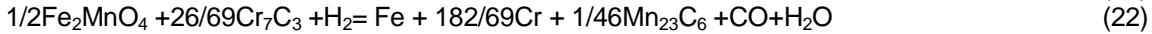
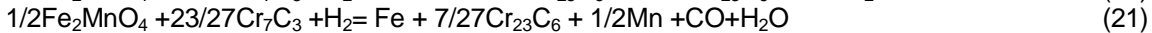
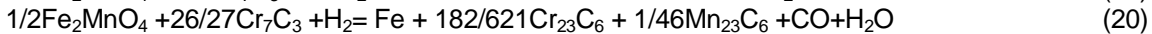
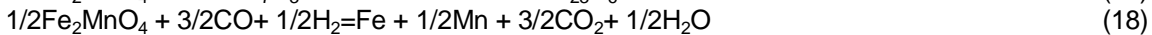
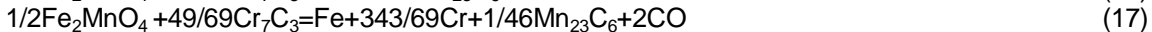
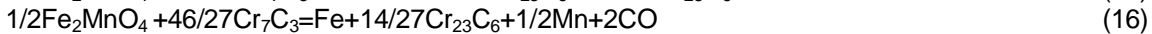
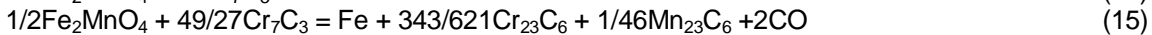
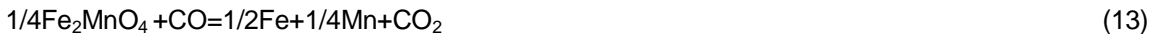
Fig. 6. Complex Fe_2MnO_4 reduction by Cr_7C_3 carbide:
 1, 2 - carbide gasification with H_2O ;
 3, 4 - ferrite reduction;
 1, 3 - $\alpha = 0.25, \beta = 0.75$;
 2, 4 - $\alpha = 0.75, \beta = 0.25$.

The results in Fig. 6 relate to the reaction of the complete reduction of manganese ferrite with chromium carbide:



However, other process schemes are possible, leading to the formation of a more complex solid product. The determining parameters in this are: temperature, the ratio O/C and C/H. We have analyzed alternative

options for both carbon-thermal and complex reduction of manganese ferrite. As possible variants, depending on the given conditions, reactions were chosen (per 1 mole of O_2):



The results of ΔG^0 calculating for the reactions 13 ... 22 are shown in Fig. 7.

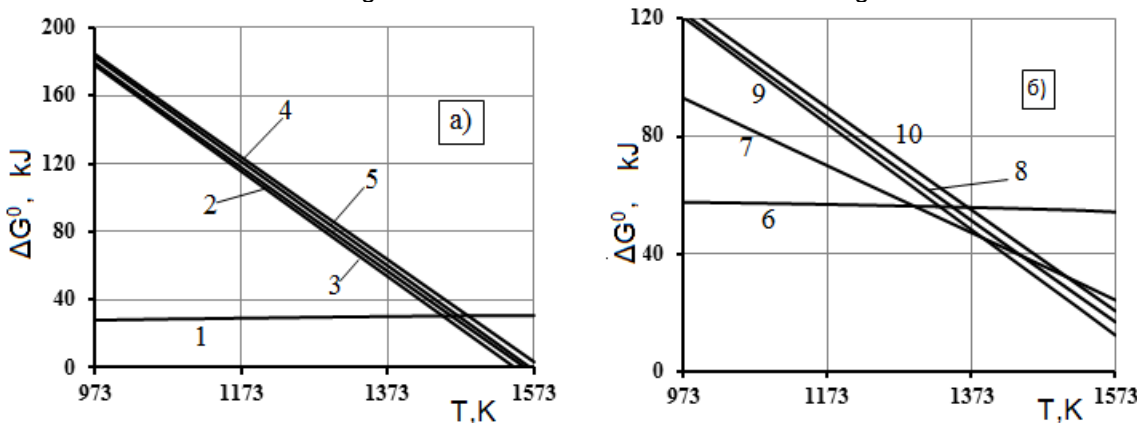


Fig. 7. Gibbs energy of the reactions of carbon-thermal (a) and complex (b) reduction of manganese ferrite with carbide Cr_7C_3 participation:
 1-10 - reactions 13 ... 22 respectively.

In the above variants, the formation of joint carbides is not taken into account as for such compounds there is no thermo-chemical data. Varying the composition of the resulting carbide phase to some extent allows us to estimate the thermodynamic probability of the formation of such carbides. The iron formed in the first stage of reduction can: replace

chromium atoms in the structure of carbide $Cr_{23}C_6$ (or Cr_7C_3), forming a joint carbide; participate in formation of Fe_3C or form a phase of Fe_{met} . The existence of Fe_{met} is thermodynamically probable until the completion of its reduction from ferrite. The beginning of manganese reduction at a sufficient temperature significantly changes the equilibrium composition of the

gas phase - the concentration of CO increases, which can trigger the formation of Fe₃C carbide by reaction $3\text{Fe} + 2\text{CO} = \text{Fe}_3\text{C} + \text{CO}_2$. However, the temperature conditions for the reduction of manganese oxide by chromium carbide and the equilibrium composition of the gas phase in this system will be prohibitive for the formation of iron carbide. If a previously reduced metal, for example, nickel, is present in the system, it is possible to form a solid solution of Ni-Fe, which is thermodynamically more preferable than the existence of Fe_{met}. However, it cannot be asserted that this variant will be more probable than the formation, by means of an isomorphous substitution, of carbide - (Cr, Fe)₂₃C₆. In this case, it is necessary to consider simultaneously two parallel processes - the transformation of the carbide phase and the reduction of the oxide, as from the physical-chemical regularities of their realization, the formation of a solid product, the ligature, depends. At complex reduction, the presence of water vapor in the system also practically excludes the existence of iron carbide. So, according to our calculations at 1273 K, the equilibrium concentration of H₂O for Fe₃C gasification, depending on the fraction (H₂ + H₂O) in the system (0.25 and 0.75), is ~ 0.283 ... 0.287%, respectively.

Comparing ΔG^0 calculation results for reactions 13-17 and 18-22, of the of manganese ferrite reduction, it should be noted a high thermodynamic preference of carbothermal process, which is related to physical-chemical features of the gasification unit. Partial replacement of carbide carbon by hydrogen, reaction 16 and 19, leads to a decrease in the thermodynamic probability in this temperature range. This feature is probably related to the difficulty of reduction at the last stage: $\text{MnO} + \text{H}_2 = \text{Mn} + \text{H}_2\text{O}$, since MnO oxide is difficult to recover for gases in comparison with carbon.

The thermodynamic advantages of carbon dioxide gasification compared to steam are also important [6].

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The change in the thermodynamic regularities in the transition from the carbon-thermal to complex reduction of Fe₂MnO₄ is illustrated by the data presented in Figure 8. The reduction of the ferrite with CO is more preferably up to ~ 1523 K, further is more thermodynamically probable the reaction of complex reduction in the H₂ stream. The latter reaction prevails at T> 1443 K and above the gas-reduction reaction by hydrogen. The complex reduction of ferrite in a hydrogen stream at T> 1233 K, is more preferable than in a CO stream. These and other thermodynamic features of the manganese ferrite reduction, in part, can be explained by the complex chemical composition of the latter. Not the last role here will belong to the accepted physical-chemical model, which would indicate the sequence of transformations.

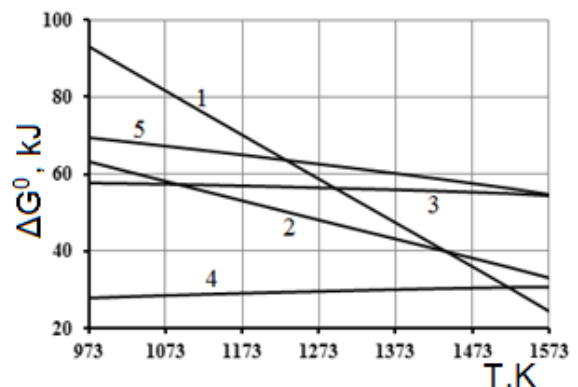


Fig.8. Temperature dependence of the Gibbs energy of the reactions:
1 – 19; 2 - 23; 3 – 18; 4 – 13; 5 – 24.

Based on the foregoing, it can be stated that it is thermodynamically possible to obtain a complex composition sponge ligature based on chromium by carbon-thermal or complex reduction of a mixture of oxides (ferrites) involving chromium carbides.

Стаття постулила: 18.09.18

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