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Thermodynamic Interaction Modeling of Periclase-Chromite Compositions with Carbon and Mixed Gases

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A thermodynamic model of interaction of periclase-chromite compositions with solid carbon and mixed reducing gases under different ratios $P_{CO}:P_{CO_2}$ at temperatures between 700 and 1400°C during anthracite calcinations in tubular rotary kilns was developed and implemented. The presence of metallic phase containing iron and chromium in the cobbing samples of periclase-chromite refractory, withdrawn from the tubular rotary kiln during its relining, was experimentally (with the use of EDX) confirmed.

Keywords: PERICLASE-CHROMITE CALCINATED COMPOSITIONS, TUBULAR ROTARY KILN, THERMODYNAMIC MODELING, REDUCTION REACTION, SOLID CARBON, CARBON OXIDE, METALLIC PHASE

Introduction

Periclase-chromite calcinated compositions (ПХСУ) are used for lining roofs of the EAF, tubular rotary kilns when calcinating cement clinker, etc. In conditions of JSC "Укрграфит" ПХСУ refractories are used for lining tubular rotary kilns during calcination of anthracite to produce thermoanthracite for coal-graphite products of wide metallurgical use. In the redox conditions of obtaining thermoanthracite created in the tubular rotary kilns, service durability of periclase-chromite lining decreases significantly compared to its resistance while using tubular rotary kilns for calcinating other types of materials. Our preliminary experimental studies of cobbings from tubular rotary kiln when calcinating anthracite fritted ПХСУ refractories showed that the mechanism of accelerated lining wear is largely determined by increasing the porosity of refractories because of reduction of iron and chromium oxides that accelerates the process of interaction of anthracite ash and pulverized coal fuel with refractory periclase-chromite lining. Therefore the object of the present study is to develop a thermochemical model of the interaction processes of periclase-chromite compositions with CO and solid carbon, and the calculation of the temperature conditions of iron reduction from magnesiowustite and chromite to iron and chromium to increase service durability of the tubular rotary kilns lining during the thermoanthracite production.

Results and Discussion

Text Thermodynamic analysis of interaction processes of calcinated periclase-chromite compositions components with solid carbon (anthracite, thermoanthracite) and gaseous CO and CO2- from tubular rotary kiln during obtaining thermoanthracite is based on the equilibrium theory of chemically reacting systems, developed by J.W. Gibbs [3, 4] and is as follows.

For the occurrence of reactions in systems written in the form

$$0 \rightleftarrows \sum_j \alpha_{ij} A_j, \quad i = 1,\ldots,r;\ j = 1,\ldots,s \qquad (1)$$

where A_j — reacting substances; α_{ij} — stoichiometric coefficient with A_j in i-th reaction (in total r reactions); coefficients are positive for products and negative for the original substances, change in the number of moles n_j of substance A_j equals

$$\Delta_i n_j = \alpha_{ij}\,\xi_i, \qquad (2)$$

here the index i with the increment symbol Δ indicates that the change refers to the execution (shift) of only one of the i-th reaction, ξ_i is a value, which does not depend on j, which is called the reaction coordinate. The number of moles of substance A_j after execution of all reactions will become equal to

$$n_j = n_j^0 + \sum \alpha_{ij}\xi_i\,, \qquad (3)$$

where n_j^0 — the amount of substance A_j before the reactions execution.

During the calculation of equilibriums it is enough to use a minimal number r of independent reactions, describing all the possible chemical processes. By independent it is meant that the reactions are with linearly independent sets of stoichiometric coefficients, i.e. those for which the rank of the matrix formed from their coefficients α_{ij}, equals r.

Besides ratios connected with the stoichiometry of reactions, there is another form of material balance accounting - through invariant linear combinations of the quantities of substances in the system. In the simplest cases it is associated with the fact of preservation of elements in chemical reactions. Namely, if a system has n elements C_j, forming s substances A_i, then the conservation law can be written in the form of equation system

$$n_j = \sum_{i=1}^{s} \alpha_{ij} n_i\,,\ j = 1,\ldots,m, \qquad (4)$$

where n_j – a number of atoms in the A_i molecule of the element C_j; n_i – a number of A_i moles.

The equilibrium conditions can be expressed in two forms: the Gibbs energy minimum of G system; mass action law equations. At constant pressure P and temperature T the equilibrium state corresponds to the minimum value of the Gibbs energy:

$$G = \sum_i n_i\left(\mu_i^0 + RT\ln N_i\right) = \min \qquad (5)$$

where n_i and N_i – a number of moles and mole fraction of i-th substance; the expression in brackets - the chemical potential; $\mu°$ – standard value of the chemical potential at P and T = const.

Minimum should be conditional, at which mass balance equation is performed. Mass balance for each component is accounted as

$$n_i^0 - \sum_i \nu_{ij} n_i = 0 \qquad (6)$$

where n_i^0 – the total number of moles of basis particles; in the sum there are taken into account all the reactions, including formal, and an unconditional extremum of the function is found.

$$\Phi = \sum_i n_i\left(\mu_i^0 + RT\ln\frac{n_i}{\sum_j n_j}\right) + \sum_i \lambda_i\left(n_j^0 - \sum_i \nu_{ij} n_i\right), \qquad (7)$$

where λ_j – Lagrange multipliers. Derivatives Φ of λ_j provide conditions for the mass balance (6).

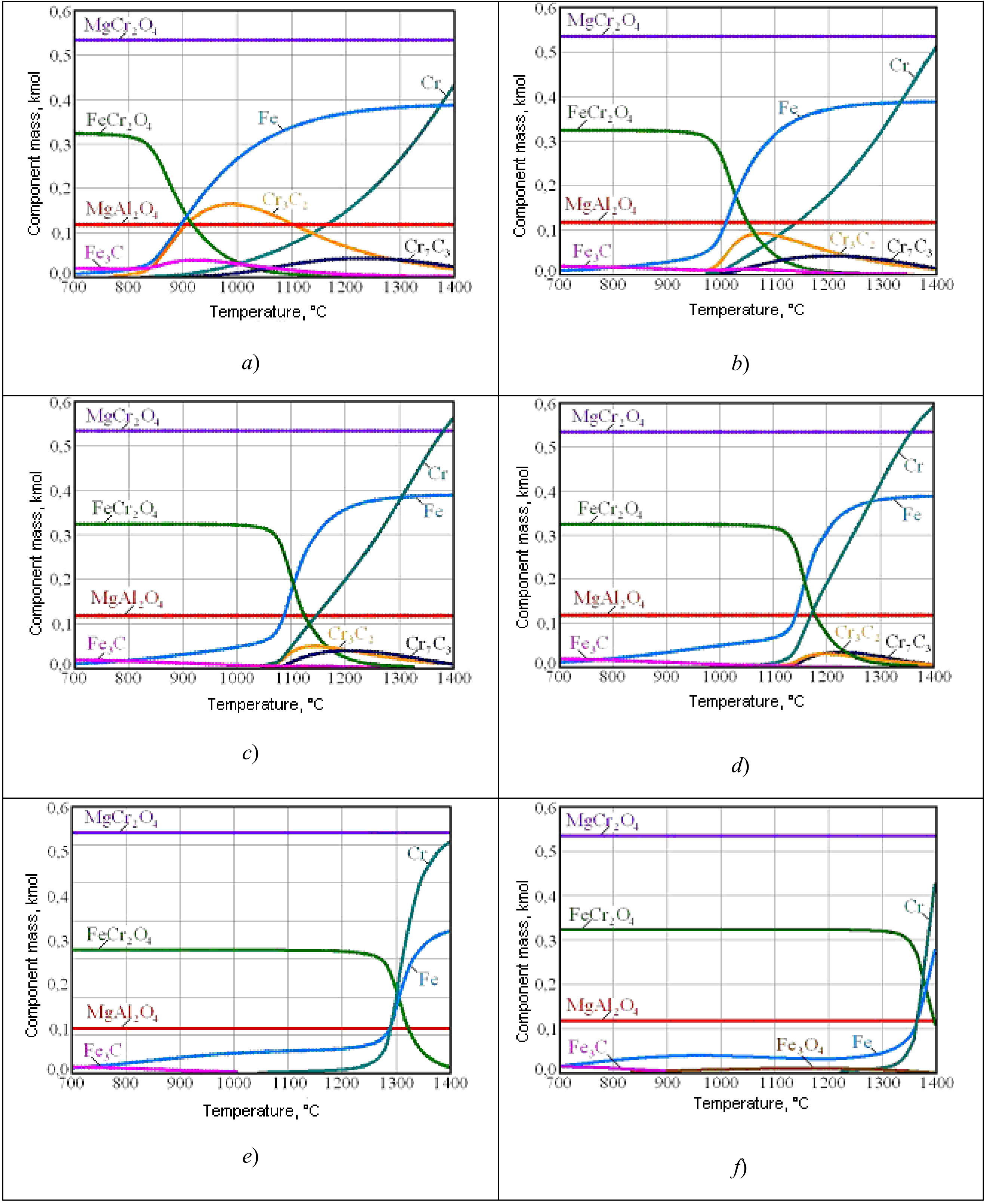
Thus, based on the data presented above and taking into account the interaction of $\ln K_k$ with the change of Gibbs energy $\Delta G^0_T = -RT\ln K_k$ the equilibrium temperature of interaction (reduction) reactions of oxide phases of the system MgO-Cr_2O_3 with solid and gaseous carbon can be calculated.

Equilibria of condensed phases of periclase-chromite calcinated composition with the gas phase of CO-CO_2 at different ratios P_{CO}/P_{CO2} in the temperature range 700-1400 ° C

Thermodynamic modeling of interaction processes of mineral phases of periclase-chromite composition (refractory) with a reducing gas phase of anthracite calcination in tubular rotary kiln was carried out by the method presented above, based on the equilibrium theory of chemically reacting systems. Thermodynamic model of equilibria calculations was implemented by means of the option Equilibrium Compositions of integrated software Outokumpu HSC Chemistry ® for Windows version 5.01. Temperature was selected as a continuously variable parameter (variability interval 700-1400 ° C); discrete variable parameter - the ratio of P_{CO}/P_{CO2} = 98/2; 97/3; 96/4; 95/5; 90/10; 85/15. The calculation results are shown in Figure 1, what allows revealing the mechanism and the sequence of iron and chromium oxides reduction with the temperature increase from 700 to 1400°C.

Reduction of FeO magnesiowustite with carbide Fe_3C formation is completed at temperatures ≤ 700°C, regardless of the redox potential of the gas phase in the considered interval of P_{CO}/P_{CO2} ratio. On the contrary, the temperature of complete reduction of chromite depends essentially on the P_{CO}/P_{CO2} ratio in the gas phase, rising from ~1000 ° C at P_{CO}/P_{CO2} = 98/2 to ~ 1400° C at P_{CO}/P_{CO2} = 90/10. When P_{CO}/P_{CO2} = 85/15 the temperature of complete reduction of chromite is ≥ 1400°C.

With decreasing the reduction potential of the gas phase the stability of iron and chromium carbides is decreased, so that when $P_{CO}/P_{CO2} \le 90/10$ and $t \ge 1000°C$, the equilibrium phases are Fe and Cr. In the range $98/2 \le P_{CO}/P_{CO2} \le 95/5$ and $850°C \le t \le 1350°C$ the equilibrium phases are Fe_3C, Cr_3C_2 and Cr_7C_3 in different ratios. In the sample of periclase-chromite composition (brick), withdrawn from the tubular rotary kiln of anthracite calcination during relining, metallic phase precipitate was discovered, representing a (according to the EDX data) eutectic, consisting of high-chromium (73,3% Cr and 26,7% Fe, dark) and high-ferrous (70,7% Fe and 29,3% Cr, light) phases containing ≤ 1% C (**Figure 2**).



a)

b)

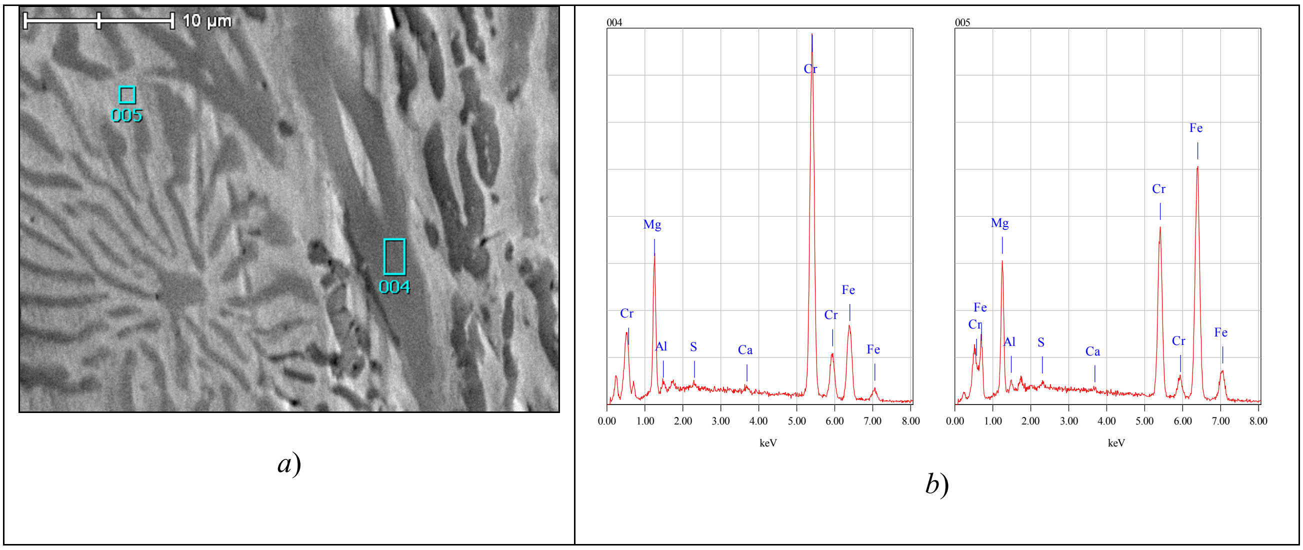
c)

d)

e)

f)

Figure 1. Equilibrium compositions of phases - products of the interaction of magnesiowustite and components of chromium ore with a reducing gas phase of anthracite calcination in tubular rotary kiln, depending on the temperature in the range 700-1400 ° C and ratio P_{CO}/P_{CO2}: *a* - 98/2; *b* - 97/3; *c*- 96/4; *d* - 95/5; *e* - 90/10; *f* - 85/15



a)

b)

Point №	Mg	Al	S	Ca	Cr	Fe	Total,%
004	8,47	0,56	0,22	0,30	66,33	24,12	100
005	8,19	0,60	0,24	0,20	26,63	64,14	100

c)

Figure 2. Microstructure of the metallic phase in the periclase-chromite refractory sample (×3500) withdrawn from the tubular rotary kiln after anthracite calcination (a) and the results of EDX phases limited by rectangles of square (b, c)

Thus, during the calcination of anthracite in the tubular rotary kiln in the temperature range 700-1400°C the development of the reduction reaction of iron from magnesiowustite (Mg, Fe)O and iron and chromium from chromite $FeO•Cr_2O_3$ of periclase-chromite compositions is obtained, what leads to the increase of porosity of the ПХСУ refractory and, consequently, its chemical and erosive wear.

Conclusions

1. Thermodynamic modeling of interaction processes of mineral phases of periclase-chromite composition (refractory) with solid carbon and a reducing gas phase of anthracite calcination in tubular rotary kiln was carried out; it was established that the reduction of FeO magnesiowustite with carbide Fe_3C formation is completed at temperatures ≤ 700°C, regardless of the redox potential of the gas phase in the considered interval of P_{CO}/P_{CO2} ratio.

2. It was shown that the temperature of complete reduction of chromite depends essentially on the P_{CO}/P_{CO2} ratio in the gas phase, rising from ~1000 ° C at P_{CO}/P_{CO2} = 98/2 to ~ 1400° C at P_{CO}/P_{CO2} = 90/10. When P_{CO}/P_{CO2} = 85/15 the temperature of complete reduction of chromite is ≥ 1400°C.

3. With decreasing the reduction potential of the gas phase the stability of iron and chromium carbides is decreased, so that when $P_{CO}/P_{CO2} \leq 90/10$ and $t \geq 1000$°C, the equilibrium phases are Fe and Cr. In the range $98/2 \leq P_{CO}/P_{CO2} \leq 95/5$ and $850°C \leq t \leq 1350°C$ the equilibrium phases are Fe_3C, Cr_3C_2 and Cr_7C_3 in different ratios.

4. The results of thermodynamic modeling were confirmed experimentally: in the sample of periclase-chromite composition (brick), withdrawn from the tubular rotary kiln of anthracite calcination during relining, metallic phase precipitate was discovered, representing a (according to the EDX data) eutectic, consisting of high-chromium (73,3% Cr and 26,7% Fe, dark) and high-ferrous (70,7% Fe and 29,3% Cr, light) phases containing ≤ 1% C

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Термодинамическое моделирование взаимодействия периклазохромитовых композиций с углеродом и газовыми смесями

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Разработана и реализована термодинамическая модель процессов взаимодействия компонентов периклазохромитовых обожженных композиций с твердым углеродом и газовыми восстановительными смесями при разных отношениях и температурах от 700 до 1400 °С применительно к условиям прокаливания антрацита в трубчатых вращающихся печах. Экспериментально (с применением РСМА) в образцах-выломках периклазохромитового огнеупора, изъятых из трубчатой вращающейся печи при ее перефутеровке, подтверждено наличие металлической фазы, содержащей железо и хром.