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THERMODYNAMIC ANALYSIS OF ELEMENTARY PROCESSES IN MOLTEN OXIDE SLAG REDUCTION

TERMODYNAMICZNA ANALIZA PODSTAWOWYCH PROCESÓW PRZY REDUKCJI CIKELYCH TLENKÓW W ŻUŻLU

The work deals with thermodynamic analysis applied to the elementary stages of the reduction of molten slag containing iron oxide. Reduction of liquid slag is possible through its interaction with solid carbon, gaseous carbon oxide and carbon dissolved in liquid iron. In the present work two chemical reactions of liquid slag with solid carbon and gaseous CO have been studied. The sets of thermodynamic equilibria in the systems: solid carbon-liquid slag-metallic iron-gas and liquid slag-metallic iron-gas were calculated by means of FACT software. Thus the simulation of the progress of reduction processes at the temperature 1800 K was obtained. The gaseous reduction products and solid iron were removed from consideration after each simulation step. The reduction with gaseous CO simulates the limiting case, where diffusion in gas is slow in comparison to surface reaction. The calculations revealed that consumption of reducing agent is much higher in the case of CO reduction. The dependences of FeO concentration in slag, CO₂ concentration in gas phase and the amount of obtained iron on the reaction progress are approximately linear in the case of reduction with carbon and parabolic in reduction with CO. The geometry of the reaction of carbon grains with slag is suggested, in which the solid carbon – slag reaction is the predominant mode of process.

Keywords: Iron oxide, molten slag, reduction, carbon, carbon oxide, thermodynamic equilibrium

Praca dotyczy analizy termodynamicznej stosowanej w podstawowych etapach redukcji ciekłych żużli zawierających tlenek żelaza. Redukcja ciekłych żużli jest możliwa przez ich współdziałanie ze stałym węglem, gazowym tlenkiem węgla i węglem rozpuszczonym w ciekłym żelazie. W tej pracy zostały zbadane dwie reakcje chemiczne ciekłego żużla ze stałym węglem i gazowym CO. Ustalenie termodynamicznych stanów równowagi w układach: stały węgiel – ciekły żużel – żelazo metaliczne – gaz oraz ciekły żużel – żelazo metaliczne – gaz zostało dokonane z wykorzystaniem oprogramowania FACT. Tym samym uzyskano symulację postępu procesów redukcji w temperaturze 1800 K. W kolejnych etapach symulacji nie rozpatrywano gazowych produktów redukcji i stałego żelaza z poprzedniego kroku. Redukcja gazowym CO symuluje proces limitujący, gdzie dyfuzja w gazie jest wolniejsza w porównaniu z reakcją na powierzchni. Obliczenia pokazują, że zużycie czynnika redukującego jest znacznie większe w procesie redukcji za pomocą CO. Zależności zawartości FeO w żużlu, zawartości CO₂ w fazie gazowej i ilości uzyskanego żelaza na postęp reakcji są w przybliżeniu liniowe w procesie redukcji węglem i paraboliczne przy redukcji za pomocą CO. Została zaproponowana geometria reakcji węgla z żużlem, w której reakcja stały węgiel – żużel jest dominującym czynnikiem procesu.

1. Introduction

The reduction of iron oxide from liquid oxide slag is the process of growing importance in pig iron production (smelting reduction) as well as in the reduction of steelmaking slags with the aim of iron oxide removal before further processing for Portland cement. The theory of iron oxide reduction in slag by means of carbonaceous materials is complex due to several possible rate-determining steps depending on temperature, slag composition and mode of reducing agent introduction. Sarma et al [1] point out, that the process takes place in

four-phase system: slag – carbon – iron (with dissolved carbon) – gas. The reactions at the phase boundaries are as follows:

- a) slag – carbon (coal, coke, charcoal)
$$\text{FeO(l)} + \text{C(s)} = \text{Fe(s/l)} + \text{CO}$$
Formation of solid or liquid Fe depends on the temperature and, to some extent on the concentration of carbon dissolved in iron.
- b) iron – carbon phase boundary
$$\text{Fe(s/l)} + \text{C(s)} = \text{Fe-C(l)}$$
Formation of solid Fe-C solution is much less probable.

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- c) slag – gas boundary
 $\text{FeO(l)} + \text{CO} = \text{Fe(s/l)} + \text{CO}_2$
- d) carbon – gas boundary
 $\text{CO}_2 + \text{C} = 2 \text{CO}$

The common view on the reduction mechanism [1–4] takes into account formation of gas layer (“halo”) around the carbon particles a result of reaction c). Thus only initial stage of carbon particle action proceeds according to the reaction a). Then the reaction c) is the predominant means of iron oxide reduction. Iron oxide participates in the both reactions and its thermodynamic activity in liquid oxide solutions influences the equilibria of reactions. The aim of the present work is the detailed analysis of the equilibria of both reactions of iron oxide reduction from liquid slag on the ground of calculations employing FACT software. From the data on the equilibrium the deeper insight into the process progress may be obtained, what allows for drawing the conclusions regarding process kinetics.

2. Thermodynamic calculations

The calculations carried out in the present work for the temperature 1800 K refer to two cases: reduction with solid carbon and with carbon oxide. In the first case – reduction of FeO in slag with solid carbon the system under consideration consists of liquid oxide solution (FeO, CaO, SiO₂, Al₂O₃), to which a portion of solid carbon is added. When thermodynamic equilibrium is reached, two new phases appear: solid iron and gaseous CO – CO₂ solution. In the adopted calculation procedure the gas phase and solid iron are removed from the system after each calculation step. New portion of solid carbon (0.5 mole) is added and new equilibrium amount and composition of phases is calculated. This cycle is repeated several times.

In the second case – reduction of FeO in slag with gaseous carbon oxide the system under consideration consists of liquid oxide solution and the CO bubble. Reaction c) of FeO reduction takes place on the liquid – gas boundary regardless of the presence the carbon particle inside the bubble. The CO bubbles without carbon particles appear as the result of reaction a). CO₂ produced in the reaction c) collects in the bubble and attains its equilibrium value. Then further reduction is inhibited. In the adopted calculation procedure the gas which attained equilibrium with liquid slag as well as produced iron is removed from the system.

The slag considered in the present work is the liquid solution of 4 components: CaO, SiO₂, Al₂O₃ and FeO. The presence of MgO is not taken into account. From the view point of steelmaking slags utilization [5] the

region of high CaO and low Al₂O₃ was chosen. As a result of introduction of solid carbon or carbon oxide into the system only FeO undergoes reduction, other components remain unchanged. The calculations were carried out for 6 slag compositions. The compositions of primary CaO-SiO₂-Al₂O₃ slags are marked in Fig. 1. Initial slag sample prior to reduction consisted of 10 moles of primary slag and 1 mole of FeO. Resulting compositions are specified in Table 1. During reduction only FeO in the sample was consumed.

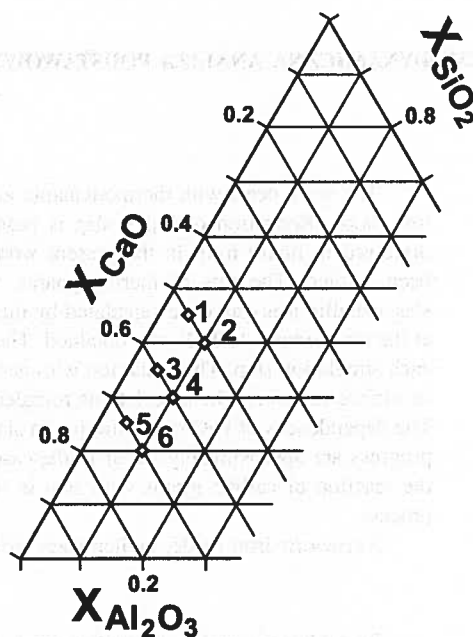


Fig. 1. Compositions of primary slags used in calculations

The calculations were carried out for the temperature 1800 K. The subsequent equilibrium compositions were determined with the use of FACT software for thermodynamic calculations.

3. Results of calculations

The results of calculations are collected in Figs. 2–5, which present the comparison of analogous dependences for two modes of reduction. Fig. 2 shows the change of FeO concentration in slag. The amounts of reducing agents used were adopted to obtain approximately equivalent reduction degree. It is striking that reduction with the use of CO consumes approximately a hundred times more carbon. The reason is obvious – the reduction with CO is terminated at the CO₂ concentration as low as 5% at most. In final stages of reduction, due to decreased amount of FeO, the equilibrium concentration of CO₂, and, consequently, the efficiency of reduction is very low. If solid carbon is the reducing agent, the formation of CO₂ does not considerably affect the course of reaction.

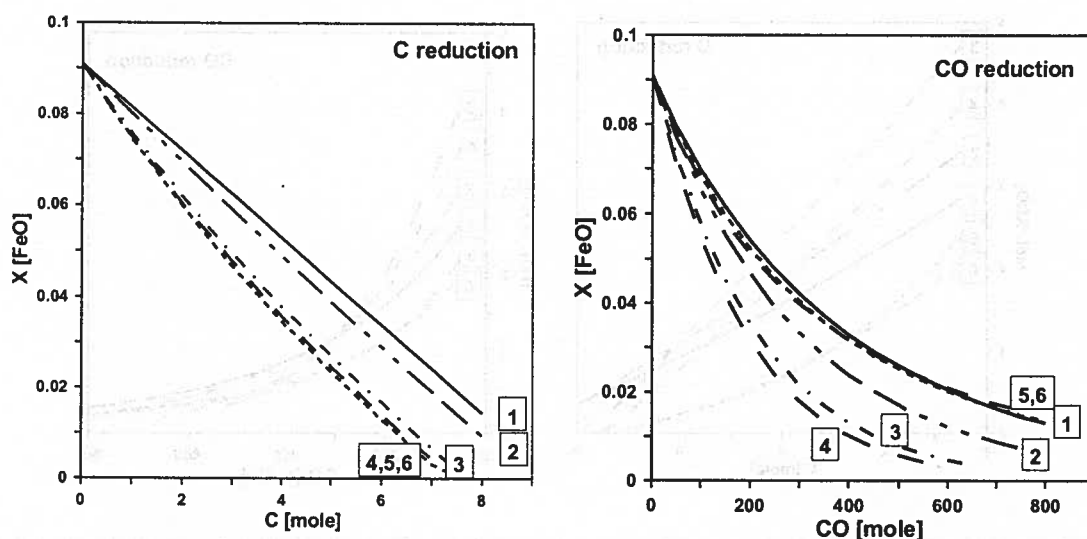


Fig. 2. Comparison of the variation of FeO concentration in slag in the course of slag reduction with solid carbon (left) and CO (right)

The question is, if such procedure reflects the real process, i.e. interaction of liquid slag with CO-CO₂ gas bubble. It may be considered as the limiting case, where the diffusion transport of CO into reaction surface and CO₂ out of reaction surface is slow in comparison to the rate of reaction c).

The FeO concentration changes almost linearly if solid carbon is used as the reducing agent. Slight deviations result from the concentration dependence of FeO activity. If gaseous CO is used as the reducing agent the action of subsequent portions of CO results in smaller amounts of reduced FeO. This effect is due to the form of equilibrium constant of reaction c), from which the FeO activity is given as:

$$a_{\text{FeO}} = \frac{P_{\text{CO}_2}}{P_{\text{CO}} \cdot K} \quad (1)$$

At lower equilibrium CO₂ pressures lower amounts of FeO are reduced. The results of simulation indicate also considerable influence of slag composition on the equilibrium of reactions of reduction. This influence reflects the dependence of FeO activity on slag composition. The calculated values of the FeO activity for its concentration $X_{\text{FeO}} = 0.0909$ are shown in Table 1.

The calculations show that at the initial stage of process the slags no 3 and 4 possess highest values of FeO activity. The lowest FeO activity values correspond to slags no 5 and 6. However, with the decrease of FeO concentration, its activity changes in different way, according to the concentrations of remaining slag components. Generally, the reduction rate is considerably higher for the slags of higher initial FeO activity (no 3 and 4). This behaviour is also reflected in Fig. 3, where for this two slag compositions the bigger slopes of P_{CO_2} curves are obtained.

TABLE 1

Slag compositions and calculated FeO activities at 1800 K

No	X[CaO]	X[SiO ₂]	X[Al ₂ O ₃]	X[FeO]	a_{FeO}
1	0.454	0.409	0.046	0.091	0.154
2	0.454	0.364	0.091	0.091	0.184
3	0.547	0.319	0.046	0.091	0.255
4	0.547	0.273	0.091	0.091	0.213
5	0.638	0.228	0.046	0.091	0.129
6	0.638	0.182	0.091	0.091	0.111

Figure 3 demonstrates the comparison of the variation of CO₂ concentration in gas phase in the course of slag reduction with solid carbon and CO. It may be stated that during reduction with solid carbon the CO₂ concentration in equilibrium with slag decreases approximately linearly, while in CO reduction the course of dependence is approximately parabolic. This effect corresponds to the variation of the amount of reduced FeO, presented in Fig. 2, which result from the form of the equilibrium constant of reaction c).

Figure 4 presents the calculated amounts of Fe₂O₃ in slag, obtained in the subsequent steps of reduction. The Fe₂O₃ presence in slag cannot be simply explained, as it should be formed according to the reaction:



which is thermodynamically improbable in the presence of CO-CO₂ gas mixture. It may be supposed; that this result may be attributed to the specific properties of databases used in FACT software. The obtained Fe₂O₃ concentrations in slag are low and they do not influence the other dependences obtained in the present work.

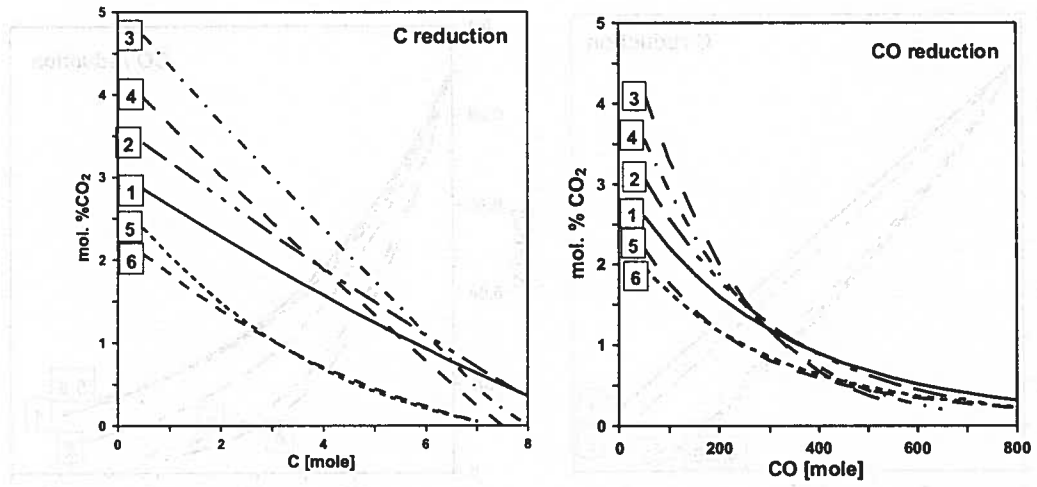


Fig. 3. Comparison of the variation of CO₂ concentration in gas phase in the course of slag reduction with solid carbon (left) and CO (right)

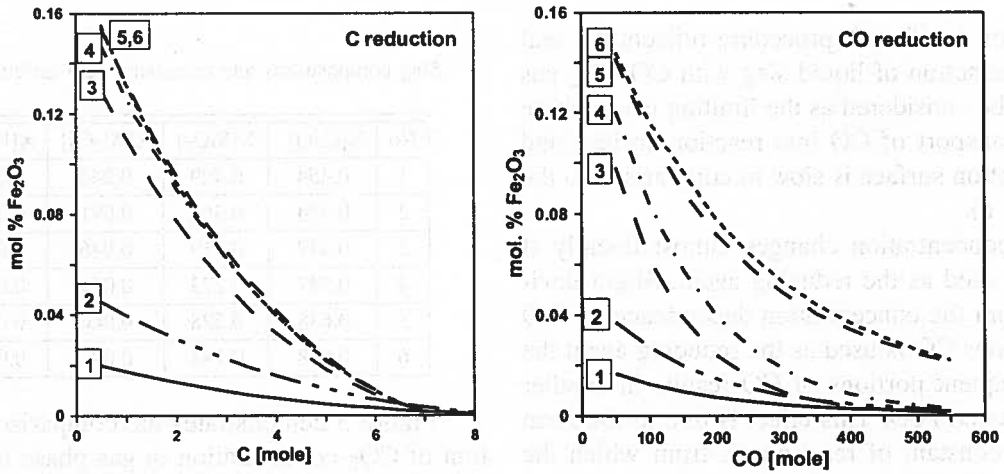


Fig. 4. Concentration of Fe₂O₃ in oxide phase during reduction with solid carbon (left) and CO (right)

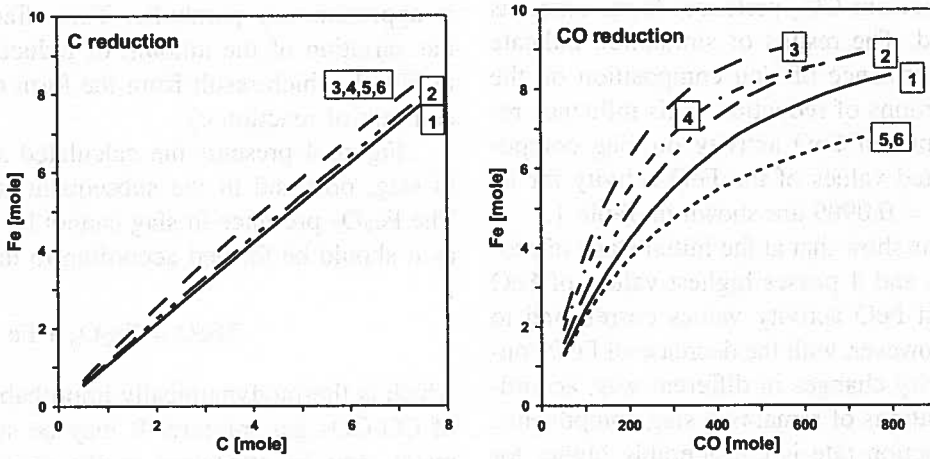


Fig. 5. Comparison of the variation of amount of reduced iron in the course of slag reduction with solid carbon (left) and CO (right)

Figure 5 presents the amount of solid iron obtained as the result of slag reduction. If solid carbon acts as the reducing agent, the amount of iron grows almost linearly. In the case of CO reduction the amount of Fe obtained in subsequent steps decreases with the progress of the process. These results are in concordance with the dependences obtained for the concentration of FeO as well as this for CO₂.

4. Discussion

The difference between reduction efficiency of C and CO demonstrated in the present work may suggest that in real process where the carbon grain size is up to 5 mm, the predominating mode is the reaction at the interface solid carbon – slag. Figure 6 presents schematically two possible situations that may appear in reduction with small carbon grains. In the scheme of process suggested by Morales et al [2] the carbon grain is enveloped with gas (Fig. 6a). We rather suggest the situation presented in Fig. 6b, where the grain of carbon floats at the slag surface. The dimensions of gas bubble may be estimated as follows. The density of carbon is approximately 2 g/cm³, while this of slag is slightly above 2.5 g/cm³ [1]. In the case of flat carbon surface the critical radius r_c of gas bubble detachment may be calculated according to [1] as:

$$r_c = \left(\frac{3 \cdot \sigma}{\rho \cdot g} \right)^{\frac{1}{2}} \quad (3)$$

where σ denotes the surface tension of slag, ρ – the density of slag and g – the acceleration of gravity.

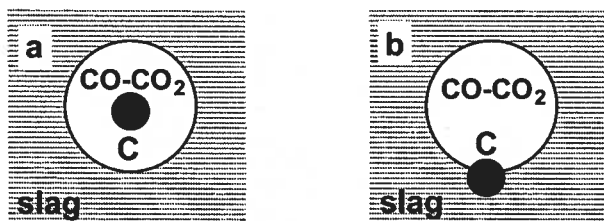


Fig. 6. Possible positions of carbon grains in gas bubble during reaction with liquid slag

The values of surface tension of oxide slag containing FeO and SiO₂ according to Morales et al [2] may be calculated from the following relation:

$$\sigma = 0.7542 - 0.5694 \cdot \left(\frac{\%SiO_2}{100} \right) - 0.1371 \cdot \left(\frac{\%FeO}{100} \right) \quad (4)$$

For the slag compositions considered in the present work, the values of slag surface tension change in the range 0.45–0.65 N/m. The critical radius, consequently,

varies in the range 0.75 to 0.9 cm. The above estimation refers to flat carbon surface. In the case of carbon particles suspended in slag larger bubbles may be expected.

The above considerations justify assumption of process geometry shown in Fig. 6b both during quiescent floating of gas bubble and during turbulent flow, where inertia forces cause the carbon particles to attach to the slag. In such case the FeO reduction proceeds simultaneously with solid carbon and CO gas. However, according to the results of the present work the solid carbon is much more active.

The calculations show that the formation of Fe-C liquid solution is impossible at the assumed geometry and the course of process, where the iron formed in reaction is removed from the system. Formation of Fe-C solution requires the direct contact of Fe and C.

5. Conclusions

Calculations of thermodynamic equilibrium for subsequent steps of reduction of oxide slag containing iron oxide, carried out in the present work, yield the simulation of elementary surface reactions in slag reduction process. It regards the variation of compositions of participating phases, omitting the real rate of the process. The considerations regard the slag reduction by means of carbon grains, as well as with gaseous CO. The calculation procedure assumes the removal of products after each step of reaction. Removal of used CO-CO₂ reducing gas after each reduction step may be equivalent to the diffusive transport of CO in the gas phase surrounding the carbon grain.

Comparison of characteristic features of both reduction modes reveals the striking difference of the amount of reducing agent needed. In the case of CO reduction the formation of equilibrium amount of CO₂ terminates the reduction process. Thus the consumption of reducing agent is much higher in this case. This effect is also responsible for parabolic shape of the curves describing the variation of concentration of FeO in slag phase and the concentration of CO₂ in gas phase.

Modelling the process of slag reduction must involve the geometry of the elementary reaction region. It is argued that the most probable position of carbon grain is at the gas – slag interface. In such case the reaction between solid carbon and slag is predominant and it mainly influences the process rate.

Acknowledgements

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3. Discussion

The reduction of iron oxide in molten slag containing iron is a complex process. It involves the reaction of iron oxide with carbon, which is injected into the slag. The reaction is influenced by the composition of the slag, the temperature, and the concentration of iron oxide. The reduction process is described by the following equation:

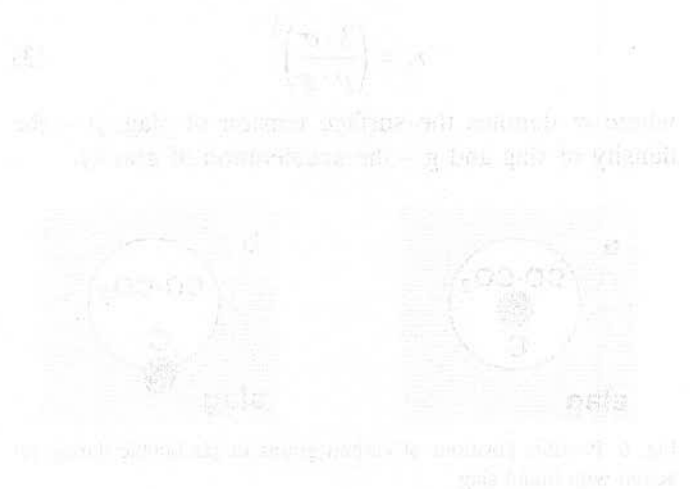
$$FeO + C \rightarrow Fe + CO$$

The rate of reduction is determined by the concentration of iron oxide in the slag and the concentration of carbon in the slag. The concentration of iron oxide in the slag is a function of the initial concentration of iron oxide and the amount of iron oxide that has been reduced. The concentration of carbon in the slag is a function of the initial concentration of carbon and the amount of carbon that has been consumed in the reduction process. The rate of reduction is also influenced by the temperature of the slag. The rate of reduction increases with increasing temperature. The rate of reduction is also influenced by the composition of the slag. The rate of reduction increases with increasing iron oxide concentration and decreasing carbon concentration. The rate of reduction is also influenced by the amount of carbon injected into the slag. The rate of reduction increases with increasing carbon injection.

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