

## METALLURGY OF NONFERROUS METALS

# Calculation of the Reduction Rate of Copper, Nickel, and Cobalt from Oxide Melts by Carbon(II) Oxide

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**Abstract**—The kinetic equation for the calculation of the reduction rate, which takes into account the physicochemical properties of contacting phases, is derived under the assumption of the electrochemical nature of interaction between the reducing gas (CO) and the oxide melt. Satisfactory agreement of calculated and experimental data is shown by the example of the interaction of the oxide melt of the CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system containing up to 6.0 wt % Me<sub>n</sub>O<sub>m</sub> (NiO, CoO, Cu<sub>2</sub>O) blown by the gas phase with partial pressure  $P_{CO} = (0.4–5.0) \times 10^2$  MPa at  $T = 1623$  K.

**Keywords:** rate calculation, reduction, oxide melt, metal cations, carbon monoxide

**DOI:** 10.3103/S1067821214030092

The interaction between the reducing gas (CO) and the oxide melt occurs in many production processes. However, there is no published procedure for calculating the reduction rate of metals by carbon monoxide from liquid slags.

In this study we derived the kinetic equation for calculating the reduction rate in the kinetic mode, which takes into account the influence of the concentration of reacting components in contacting phases.

### QUALITATIVE PATTERN OF INTERACTION OF OXIDE MELT WITH THE GAS PHASE

The interaction of the oxide melt containing metal cations of the transient group (copper, nickel, cobalt, etc.) with carbon monoxide probably follows the electrochemical mechanism. This is indicated by the following notions.

First, according to the modern viewpoint [1, 2], preferentially oxygen ions are arranged in the surface layer of oxide melts, while metal cations are displaced into the depth of the liquid phase; i.e., a peculiar electric microcapacitor is formed. In this case the potential jump is localized not on both sides of the physical phase interface, as is observed for the exchange mechanism of the formation of a double electric layer (DEL) at the metal–oxide melt boundary, but inside the oxide phase. The negative plate of the DEL that appears here is arranged nearer to the interface with the gas phase, while the positive plate is shifted from it into the melt depth.

Second, carbon monoxide molecules are adsorbed from the gas-phase side. A double electric layer promotes the electron transition from CO molecules to

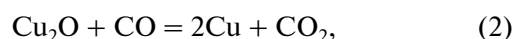
metal cations. Formed CO<sup>2+</sup> ions are arranged near oxygen cations and form strong chemical bonds with them. The appearing energetic relationships in the system are such ( $G < 0$ ) that the (CO<sup>2+</sup>O<sup>2-</sup>) complex transforms into an adsorbed molecule with closed chemical bonds which is kept on the melt surface by relatively weak intermolecular bonds.

### DERIVATION OF THE KINETIC EQUATION

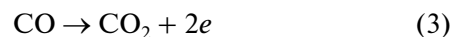
Let us write the reduction reaction of metal cations in a liquid slag by carbon monoxide in the general form:



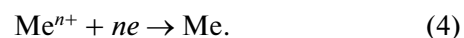
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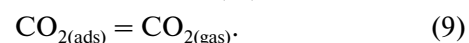
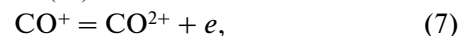
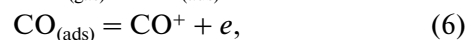
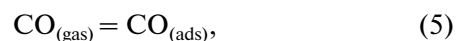
Let us assume that reaction (1) consists of two half-reactions, notably, the anodic one



and the cathodic reaction, which passes to metal:



We accept that anodic oxidation of CO molecules involves the following stages in the case under consideration:



Stages (5), (8), and (9) are chemical stages. In our opinion, they do not limit general reduction process (1), while (6) and (7) are electrochemical reactions. We will consider that half-reaction (6) is the retarded stage, while stage (7) proceeds reversibly.

When deriving the kinetic equation to calculate the process rate, we used data [3] as well as the Langmuir adsorption isotherm, which makes it possible to involve free and occupied vacancies at the phase interface into the number of reagents participating in oxidation. Their formal activities can be expressed through the filling degree ( $\theta$ ).

Applying the Nernst equation to reversible stage (9), let us find  $\theta/\theta_e$  and  $(1-\theta)/(1-\theta_e)$ :

$$\varphi = \varphi^0 + \frac{RT}{F} \ln \frac{\theta}{1-\theta}, \quad (10)$$

$$\varphi_e = \varphi^0 + \frac{RT}{F} \ln \frac{\theta_e}{1-\theta_e}, \quad (11)$$

where  $\varphi^0$  and  $\varphi_e$  are the standard and equilibrium potentials and  $F$  is the Faraday constant.

The polarization anodic characteristic ( $\eta_a$ ) is determined by the difference between  $\theta$  and  $\theta_e$ :

$$\eta_a = \varphi_e - \varphi = \frac{RT}{F} \ln \frac{\theta_e}{1-\theta_e} \frac{1-\theta}{\theta}. \quad (12)$$

From expression (12), we derive

$$\theta = \frac{\theta_e \exp\left(\frac{F}{RT} \eta_a\right)}{1-\theta_e + \theta_e \exp\left(\frac{F}{RT} \eta_a\right)}. \quad (13)$$

According to the retarded discharge theory [4] and allowing for Eq. (13), we can write for the rate of process (6)

$$\begin{aligned} i_{(6)} \frac{1}{F} &= \overset{\rightarrow}{k} \theta_e \exp\left(\frac{\alpha F}{RT} \varphi\right) \\ &= \overset{\leftarrow}{k} (1-\theta) \exp\left(-\frac{(1-\alpha)F}{RT} \varphi\right), \end{aligned} \quad (14)$$

where  $\alpha$  is the transfer coefficient and  $\overset{\rightarrow}{k}$  and  $\overset{\leftarrow}{k}$  are the rates of the forward and reverse processes.

To simplify expressions (14) in the equilibrium state, let us use the magnitude of exchange current ( $i_0$ ):

$$\begin{aligned} i_{0(6)} \frac{1}{F} &= \overset{\rightarrow}{k} \theta_e \exp\left(\frac{\alpha F}{RT} \varphi_e\right) \\ &= \overset{\leftarrow}{k} (1-\theta_e) \exp\left(-\frac{(1-\alpha)F}{RT} \varphi_e\right). \end{aligned} \quad (15)$$

Dividing Eq. (14) by (15), we derive

$$\begin{aligned} i_6 &= i_{0(6)} \left[ \frac{\theta}{\theta_e} \exp\left(\frac{\alpha F}{RT} \eta_a\right) \right. \\ &\quad \left. - \frac{1-\theta}{1-\theta_e} \exp\left(-\frac{(1-\alpha)F}{RT} \eta_a\right) \right]. \end{aligned} \quad (16)$$

Using relationships (12) and (13), we exclude quantity  $\theta$  from Eq. (16); in addition, we will take into account that the degree of filling the surface is invariable with time in steady-state conditions; i.e., the formation rate of adsorbate particles equals their discharge rate:

$$i_{(6)} = i_{(7)}, i = i_{(6)} + i_{(7)} = 2i_{(6)}. \quad (17)$$

The transformed kinetic equation gives the  $\eta$  dependence of  $i$  in an explicit form:

$$\begin{aligned} i &= i_{0(6)} \frac{\exp\left(\frac{(1+\alpha)F}{RT} \eta_a\right)}{1-\theta_e + \theta_e \exp\left(\frac{F}{RT} \eta_a\right)} \\ &\quad - i_{0(6)} \frac{\exp\left(-\frac{(1-\alpha)F}{RT} \eta_a\right)}{1-\theta_e + \theta_e \exp\left(\frac{F}{RT} \eta_a\right)}, \end{aligned} \quad (18)$$

where  $i_{0(6)}$  is the doubled exchange current for process (6).

For the subsequent analysis of reaction (1), we should reveal the dependence of quantity  $i_0$  on the partial pressure of carbon monoxide in the gas phase. We will derive it excluding  $\varphi_e$  from Eq. (15) and expressing  $\theta_e$  through  $P_{CO}$  and equilibrium constant of the following reaction:



$$K_{P(19)} = \frac{\theta_e^2}{P_{CO}(1+\theta_e)^2}. \quad (20)$$

$$\theta_e = \frac{(K_{P(19)} P_{CO})^{1/2}}{1 + (K_{P(19)} P_{CO})^{1/2}}. \quad (21)$$

After the substitution and transformations for the magnitude of the exchange current, we derive the following expression:

$$i_0 \approx \frac{K_{P(19)} P_{CO}^{(2-\alpha)/2}}{1 + (K_{P(19)} P_{CO})^{1/2}}. \quad (22)$$

The influence of the partial pressure of CO in the gas phase on parameter  $i_0$  is determined by the deviation of product  $(K_{P(19)} P_{CO})^{1/2}$  from unit: if it is larger than unit, then  $i_0 \sim (P_{CO})^{(1-\alpha)/2} \sim (P_{CO})^{0.25}$  and, with the inverse ratio,  $i_0 \sim (P_{CO})^{(2-\alpha)/2} \sim (P_{CO})^{0.75}$ . Here,

Kinetic interaction parameters of the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Me}_n\text{O}_m$  oxide melt with the reducing gas (CO) at  $T = 1623 \text{ K}$

$\text{Me}_n\text{O}_m$ , mass %	$P_{\text{CO}}$ , atm	Order of reaction by concentration				Reaction rate $v \times 10^{12}$ , $\frac{\text{mol}_{\text{Me}_n\text{O}_m}}{\text{m}^2 \text{ s}}$	
		$\text{Me}_n\text{O}_m$		CO			
		Experiment	Calculation	Experiment	Calculation	Experiment	Calculation
3.7 $\text{Cu}_2\text{O}$	0.195	0.60	0.75	0.85	1.0	5.0	4.6
5.8 NiO	0.6	0.80	0.75	0.90	1.0	8.0	3.0
5.7 CoO	0.6	0.80	0.75	0.90	1.0	6.5	4.3

transfer coefficient  $\alpha$  for evaluating calculations is accepted to be 0.5.

The polarization characteristic for the cathode reduction of metal ions ( $\eta_c$ ) is

$$\eta_c = \frac{RT}{zF} \ln(1 - i/i_l), \quad (23)$$

where  $i_l$  is the limiting diffusion current of metal cations to the gas–melt interphase boundary and  $z$  is the number of electrons.

The algebraic sum of polarizations ( $\eta_a$  and  $\eta_c$ ) determines the total deviation of the gas–oxide melt system from the equilibrium:

$$\eta_a - \eta_c = -\frac{\Delta G}{zF} = \frac{RT}{zF} \ln \frac{K_p}{\Pi a}, \quad (24)$$

where  $\Pi a$  is the product of activities.

We derive the formula for the reduction rate from Eqs. (18), (23), and (24):

$$v = \frac{i}{zF} = \frac{i_0}{zF} \left[ \left( \frac{K_{p(1)}}{\Pi a_{(1)}} \right)^{\frac{1+\alpha}{2}} \left( 1 - \frac{i}{i_l} \right)^{\frac{1+\alpha}{2} qn} - \left( \frac{K_{p(1)}}{\Pi a_{(1)}} \right)^{\frac{1-\alpha}{2}} \left( 1 + \frac{i}{i_l} \right)^{\frac{1-\alpha}{2} qn} \right]. \quad (25)$$

At large equilibrium constants of process (1), we can neglect the reverse reaction, i.e., neglect the second summand in Eq. (25):

$$v = \frac{i_0}{zF} \left[ \left( K_{p(1)} \frac{a_{\text{Me}_n\text{O}_m}^q P_{\text{CO}}^m}{P_{\text{CO}_2}^m} \right)^{\frac{1+\alpha}{2}} \left( 1 - \frac{i}{i_l} \right)^{\frac{1+\alpha}{2} qn} \right]. \quad (26)$$

At the initial interaction stages of the oxide melt with the reducing gas, the process mode is close to kinetic. In this case, expression (26) takes the form

$$v = \frac{i_0}{zF} \left( K_{p(1)} \frac{a_{\text{Me}_n\text{O}_m}^q P_{\text{CO}}^m}{P_{\text{CO}_2}^m} \right)^{(1+\alpha)/2}. \quad (27)$$

Let us consider certain consequences following from formula (27).

For the interaction of univalent oxide with CO (for example,  $\text{Cu}_2\text{O}$ ), indices of equation of reaction (1) are as follows:  $q = 1$ ,  $n = 2$ , and  $m = 1$ . Then Eq. (27) takes the form

$$v = v_0 \left( K_{p(1)} \frac{a_{\text{Me}_n\text{O}_m} P_{\text{CO}}}{P_{\text{CO}_2}} \right)^{(1+\alpha)/2}. \quad (28)$$

Separating the concentration dependence of the reduction rate on  $\text{Me}_2\text{O}$ , we see that

$$v \sim C_{\text{Me}_2\text{O}}^{(1+\alpha)/2} \sim C_{\text{Me}_2\text{O}}^{0.75}. \quad (29)$$

The influence of the partial pressure of carbon monoxide on quantity  $v$ , allowing for  $i_0 \sim P_{\text{CO}}^{0.25}$ , turns out in the first extent ( $v \sim P_{\text{CO}}$ ).

For the interaction of divalent oxide with CO (for example, CO, NiO, etc.), indices of equation of reaction (1) are equal:  $q = 1$ ,  $n = 1$ , and  $m = 1$ . In this case, expression (27) takes the form

$$v = v_0 \left( K_{p(1)} \frac{a_{\text{MeO}} P_{\text{CO}}}{P_{\text{CO}_2}} \right)^{(1+\alpha)/2}, \quad (30)$$

i.e., the dependence of  $v$  on the MeO concentration and  $P_{\text{CO}}$  is the same as for the univalent oxide:

$$v \sim C_{\text{MeO}}^{0.75} \text{ and } P_{\text{CO}}.$$

## REDUCTION OF METALS IN OXIDE MELTS BY CARBON MONOXIDE

To calculate the reduction rate of metals in oxide melts according to the proposed equations, we should know the exchange current ( $i_0$ ). The evaluation of this quantity is presented in [5] and constitutes  $7.2 \times 10^{-13} \text{ mol}/(\text{m}^2 \text{ s})$  for temperature 1573 K.

The table represents the experimental data taken from [6–8], where the interaction kinetics of reducing gas (CO) with oxides of copper(I), nickel(II), and cobalt(II) at their concentrations up to 6 wt % in  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  melts was investigated by the ideal mixing of the gas flow. It was established that the transformation of oxides to metal occurs in the kinetic mode. The comparison of theoretical and experimental values of the reaction order by concentrations of

CO and  $Me_nO_m$  and reduction rates show their satisfactory agreement.

### CONCLUSIONS

Starting from the electrochemical nature of interaction between carbon monoxide and the oxide melt, kinetic equation (29) was proposed to calculate the reduction process in the kinetic mode, which takes into account the influence of the concentration of reacting components in contacting phases.

### ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 11-08-12062.

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*Translated by N. Korovin*