JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 147–151

Electroanalysis of iron in molten slags

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Received 13 April 1976

It has been found, using chronopotentiometry, that ferric and ferrous ions in sodium disilicate at 950° C act as separate reducible species. The electrode processes have been examined and the diffusion coefficients have been determined.

Using known weights of ferric oxide and ferrous oxalate in sodium disilicate glass, calibration curves have been obtained. These gave a good agreement between experimental and estimated values for mixtures of ferric and ferrous ions and suggest that the electroanalytical method could be suitable for the examination of ferric/ferrous ratios in steel-making slags.

1. Introduction

It is often important to know the Fe^{3+}/Fe^{2+} ratios in steelmaking slags and the chemical analytical methods are complicated. One method requires the solution of the glass under nitrogen to prevent oxidation and alteration of the ratios. The Fe^{2+} is then measured by quantitative oxidation and the total iron is determined colorimetrically.

Work on the diffusion of a number of metal ions in sodium disilicate over a temperature range of 900–1000° C [1] indicated that the ferric ion was not reduced to ferrous on electroreduction at the cathode. The technique employed was chronopotentiometry or voltammetry at constant current, in which the transition time τ is related to other variables by the Sand equation

$$i\tau^{1/2} = \tfrac{1}{2}\pi^{1/2}FnD^{1/2}C \qquad (1)$$

where i = current density; C = concentration of the reducible species; D = diffusion coefficient and n = number of electrons involved.

Using this method the possibility of analysing ferrous–ferric mixtures was explored.

2. Experimental

2.1. *Apparatus*

Constant current conditions were obtained from a 350 V Farnell stabilized voltage supply with a variable voltage range, applied to a 10 000 Ω resistance box in series with the electrolysis cell. The electrolysis cell consisted of a graphite or platinum crucible acting as a non-polarizable anode and a 2 mm diameter tungsten rod used as the micro-cathode. The cell was placed in a closed-end silica tube through which argon was passed and the assembly was heated in a vertical tube furnace.

2.2. *Preparation of solutions*

Solutions of ferric ions were made by adding ferric oxide to sodium disilicate and melting. The prepared glass was ground, remelted and reground to ensure homogeneity. For ferrous solutions, anhydrous ferrous oxalate was added to the silicate and the mixture was heated under argon. Subsequent remelting was also carried out under argon.

Samples of varying concentration (up to about 6%) were prepared in this way. Mixed ferrous–ferric glasses were made by mixing the appropriate amounts of each glass, melting under argon and regrinding.

2.3. *Electrolysis of molten glasses*

Glasses containing varying concentrations of either ferrous or ferric ions were electrolysed at 950° C in an argon atmosphere. The current was increased until a transition occurred and the transition times were determined with further increases of current. The cathode potential was displayed on a storage oscilloscope Tetronix 564 and recorded on a Polaroid film. The transitions were also examined by using an X–Y recorder.

From the variation of $i\tau^{1/2}$ values, the diffusion coefficients can be determined if the number of electrons n involved in the reduction is known. For a reversible reaction with soluble products the potential of the electrode for the diffusion process is given by the following relationship:

$$E = E_{\tau/4} - \frac{RT}{nF}\log_e \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \qquad (2)$$

where $E_{\tau/4}$ is the reduction potential of the ion. From the slope of E versus $\log_e(\tau^{1/2} - t^{1/2})/t^{1/2}$ the value of n can be determined.

3. Results and discussion

3.1. *Electrode processes*

Using solutions of ferrous or ferric ions, single transitions were obtained with current densities which kept the cathode potential below − 1·0 V (reduction potential of orthosilicate ion). Typical chronopotentiograms are shown in Figs. 1 and 2. Transition times obtained for 2% ferric oxide and 5% ferrous oxalate additions are shown in the following tables.

Using Equation 2, the variation of cathode potential with time was plotted taking the data from a number of chronopotentiograms. Typical results are shown in Fig. 3, giving values of 3 and 2 for the ferric and ferrous ion respectively. It can also be seen that the ferric ion is reduced at a potential of about 40 mV more anodic than the ferrous ion compared with graphite.

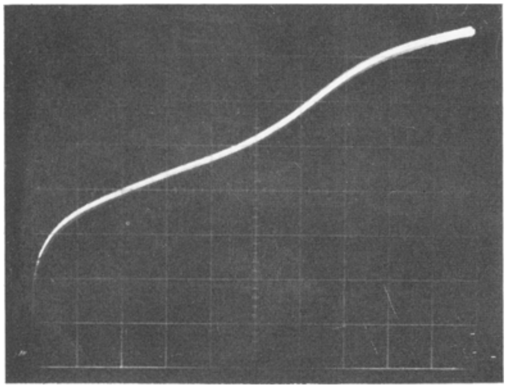

Fig. 1. Ferric oxide in sodium disilicate at 950° C.

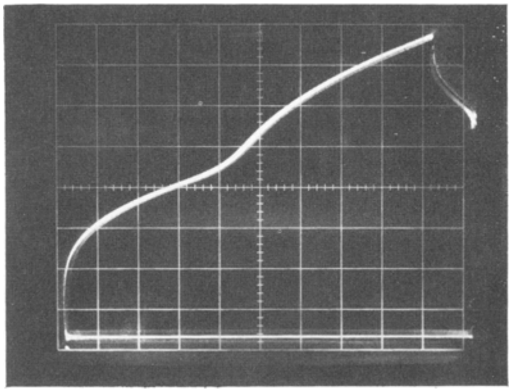

Fig. 2. Ferrous oxalate in sodium disilicate at 950° C

Table 1. 2% Ferric oxide in sodium disilicate. Temperature 950° C*; area of electrode* 0·41 cm^2

i(mA)	τ(s)	$\tau^{1/2}$	$i\tau^{1/2}$ (mA s$^{1/2}$)
12·0	8·0	2·83	34·0
15·0	5·4	2·32	34·8
17·0	4·3	2·05	35·3
20·0	3·0	1·73	34·6
25·0	2·0	1·41	35·2
31·0	1·3	1·14	35·3
35·0	1·0	1·00	35·0
		Average	34·9

$i\tau^{1/2} = 8{\cdot}5 \times 10^{-2}$ (A cm^{-2} s$^{1/2}$).

Table 2. 5% Ferrous oxalate in sodium disilicate. Temperature 950° C*; area of electrode* 0·19 cm^2

i(mA)	τ(s)	$\tau^{1/2}$(s)	$i\tau^{1/2}$ (mA s$^{1/2}$)
15·0	2·3	1·52	22·7
20·0	1·3	1·14	22·8
25·0	0·80	0·89	22·3
30·0	0·53	0·73	21·9
34·0	0·43	0·66	22·3

$i\tau^{1/2} = 11{\cdot}8 \times 10^{-2}$ A cm^{-2} s$^{1/2}$.

The single three-electron step for the ferric ion is unexpected since the behaviour in aqueous solutions corresponds to the reduction to the ferrous state followed by a further reduction to iron. However, electron spin resonance spectra for iron oxide additions for glasses up to 5% have indicated that ferric oxide gives a tetrahedral structure [2]. The ferric glasses were produced under normal atmospheric conditions and it is possible that the ferrate

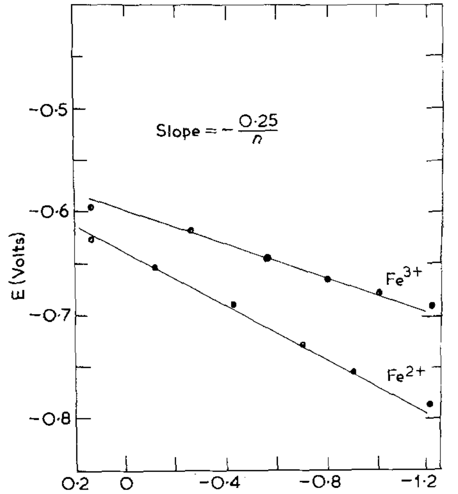

Fig. 3. E versus $\log_{10}(\tau^{1/2}-t^{1/2})/t^{1/2}$.

ion FeO_4^{2-} is formed. In these circumstances the reduction process could correspond to

$$FeO_4^{2-}+3e = Fe^{3+}+4O^{2-}. \qquad (3)$$

Since the potential of the micro-electrode was allowed to reach ground state conditions before the next pulse was applied, this could allow the ferric ion produced to return to its original structure. In order to investigate the possibility of the ferric to ferrous reduction, samples of ferrous glasses prepared as above were first oxidized at the micro-electrode and the current was reversed immediately after the transition occurred. A typical chronopotentiogram is shown in Fig. 4. From the variation of charging potential with time it was established that the oxidation corresponded to a one-electron process, i.e. formation of ferric ions. The ratio of the transition times for the oxidation and reduction steps was 3 : 1. This is the criterion for a reversible process [3] and would seem to indicate that the ferric ion produced in these circumstances can be reduced to the ferrous state.

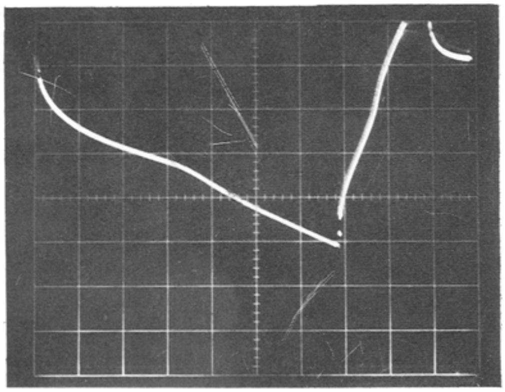

Fig. 4. Oxidation and reduction of ferrous in sodium disilicate at 950° C.

3.2. *Diffusion coefficients*

The values of $i\tau^{1/2}$ for varying concentrations of ferric oxide and ferrous oxalate are shown in Fig. 5. The corresponding concentrations of ferric and ferrous ions are also shown. The percentage weights were converted into mol cm^{-3} using a value of 2·30 g cm^{-3} for sodium disilicate at 950° C as quoted by Bockris *et al.* [4]. This gives values of $1{\cdot}44\times10^{-4}$ mol cm^{-3} and $1{\cdot}60\times10^{-4}$ mol cm^{-3} for 1% of ferric oxide and ferrous oxalate respectively; results are shown in Fig. 6. The diffusion coefficients (D) can be calculated from the slopes and values obtained for the ferric and ferrous additions were 0·30 and $0{\cdot}70\times10^{-6}$ cm^2 s^{-1} respectively.

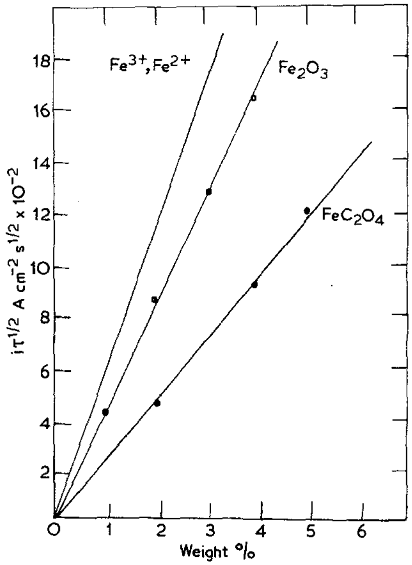

Fig. 5. Solutions in $Na_2Si_2O_5$.

It can be seen from Fig. 5 that equal percentage concentration of ferric and ferrous ions give the same $i\tau^{1/2}$ values.

Let τ_1 and τ_2 be the transition times for the ferric and ferrous ions respectively. From the Sand equation equal values of $i\tau^{1/2}$ would be given for

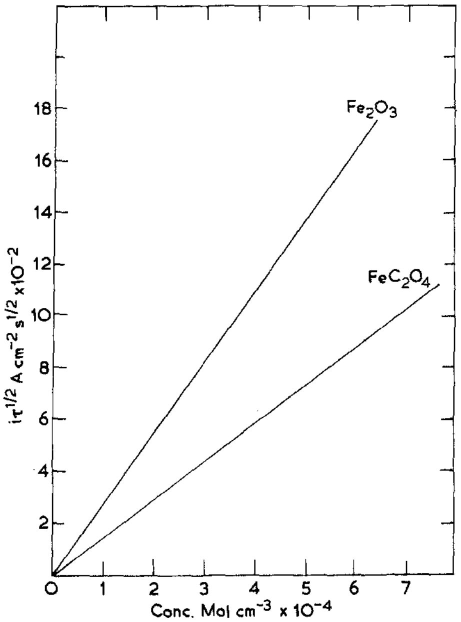

Fig. 6. Solutions in sodium disilicate.

$\frac{1}{2}\pi^{1/2}Fn_1D_1^{1/2}C_1 = \frac{1}{2}\pi^{1/2}Fn_2D_2^{1/2}C_2$. But C_1 and C_2 are equal for equal percentage weights. That is $n_1D_1^{1/2} = n_2D_2^{1/2}$ or $n_1/n_2 = (D_2/D_1)^{1/2} = (0{\cdot}7/0{\cdot}3)^{1/2} = 1{\cdot}53$. This supports the values of $n_1 = 3$ and $n_2 = 2$ obtained above.

3.3. *Ferric–ferrous mixtures*

Having established the n and D values for glasses containing ferric or ferrous ions, mixtures of these glasses were electrolysed. Two transitions were observed at potentials less cathodic than that required to reduce the orthosilicate anion, Fig. 7. If it is assumed that the ions act as independent species the transition time relationships for τ_1 (ferric) and τ_2 (ferrous) become

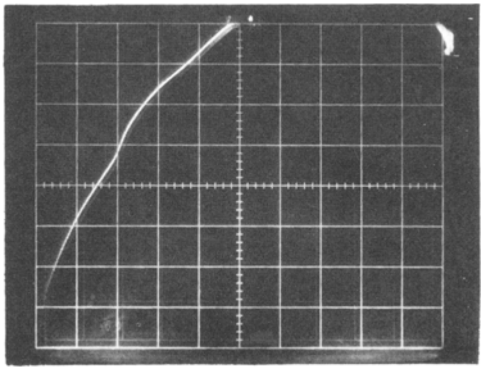

Fig. 7. Mixture of ferric and ferrous in sodium disilicate at 950° C.

$$i\tau_1^{1/2} = \tfrac{1}{2}\pi^{1/2}Fn_1D_1^{1/2}C_1, \quad (4)$$

$$i[(\tau_1+\tau_2)^{1/2} - \tau_1^{1/2}] = \tfrac{1}{2}\pi^{1/2}Fn_2D_2^{1/2}C_2. \quad (5)$$

Thus for a particular mixture of ferric–ferrous ions the values of $i\tau_1^{1/2}$ and $i[(\tau_1+\tau_2)^{1/2} - \tau_1^{1/2}]$ should be constant. Results are shown in Table 3 for a glass containing 4% ferric oxide and 2% ferrous oxalate.

Using Fig. 5 the values of 16·6 and 4·2 × 10^{-2} A cm^{-2} give 3·9% ferric oxide and 1·9% ferrous oxalate.

3.4. *Slag samples*

Samples of iron made up in an artificial lime–alumina slag were obtained from the British Steel Corporation. These contained various concentrations of total iron up to 10%. Three types of glass were supplied (a) all ferric; (b) ferric to ferrous ratios of 2 : 1; and (c) ferric to ferrous ratios of 1 : 2. Samples (b) and (c) containing 10% total iron were made up as 20% solutions in

Table 3. Sodium disilicate with 4% ferric oxide, 2% ferrous oxalate. Temperature 950° C; *area of electrode* 0·18 cm^2.

i(mA)	τ_1 (s)	$(\tau_1+\tau_2)$(s)	$i\tau_1^{1/2}$	$i(\tau_1+\tau_2)^{1/2}$	$i[(\tau_1+\tau_2)^{1/2} - \tau_1^{1/2}]$
12·0	6·0	9·5	29·4	37·0	7·6
14·0	4·5	7·2	29·7	37·6	7·9
19·0	2·5	4·0	30·0	38·0	8·0
24·0	1·6	2·6	30·2	38·7	7·6
		Average	29·9	37·8	7·6
			16·6 × 10^{-2} (A cm^{-2} s$^{1/2}$)	21·0 × 10^{-2} (A cm^{-2} s$^{1/2}$)	4·2 × 10^{-2} (A cm^{-2} s$^{1/2}$)

Table 4. Fe^{3+}:Fe^{2+} From X–Y plots

Samples	$^*\tau_1$	$^*\tau_1 + \tau_2$	$\tau_1^{1/2}/(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2}$
(b) 2 Fe^{3+} : 1 Fe^{2+}	7·0	16·0	1·96
	7·7	15·2	2·06
	4·3	10·0	1·90
(c) 1 Fe^{3+} : 2 Fe^{2+}	1·3	10·7	0·53
	2·0	16·3	0·54

* Values measured as cm along time axis

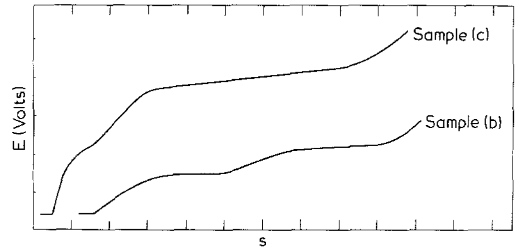

Fig. 8. X–Y plots.

sodium disilicate under argon atmosphere. The samples were then allowed to cool and reground. The prepared glasses were electrolysed as above and the transitions displayed on the Tetronix oscilloscope. At a suitable current density, with transition times of the order of seconds, the cathode potential was applied to an X–Y recorder. Typical curves are shown in Fig. 8. Using Equations 4 and 5:

$$\frac{i\tau_1^{1/2}}{i[(\tau_1+\tau_2)^{1/2}-\tau_1^{1/2}]} = \frac{n_1 D_1^{1/2} C_1}{n_2 D_2^{1/2} C_2}.$$

If it is assumed that the D values are as above then $n_1 D_1^{1/2} = 1{\cdot}62 \times 10^{-3}$ and $n_2 D_2^{1/2} = 1{\cdot}68 \times 10^{-3}$. Taking these as equal:

$$\frac{C_1}{C_2} = \frac{\tau_1^{1/2}}{(\tau_1^{1/2}+\tau_2^{1/2})-\tau_1^{1/2}} \tag{6}$$

and

$$\frac{C_1}{C_1+C_2} = \frac{\tau_1^{1/2}}{(\tau_1+\tau_2)^{1/2}}. \tag{7}$$

Thus the concentration ratios of ferric to ferrous and ferric to total iron can be obtained. Results for ferric to ferrous ratios are shown in Table 4.

4. Conclusions

(a) Ferric and ferrous ions in molten sodium disilicate behave independently when reduced at a micro-electrode.

(b) A slag containing a certain ratio of ferric to ferrous ions appears to retain this ratio when the slag is dissolved in sodium disilicate.

(c) Chronopotentiometry offers an analytical procedure for the determination of ferric to ferrous ratios and total iron in slags.

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