Rates of oxygen removal from titaniferous oxide melts in graphite crucibles*

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SYNOPSIS

Slags of the system $CaO–MgO–Al_2O_3–TiO_2–SiO_2$ that had been reduced in graphite crucibles for selected time intervals were fully re-oxidized so that an assessment could be made of the rate and extent to which the titanium oxide had been reduced. The derived kinetic parameters were studied as functions of slag composition and temperature. The extent of reduction after selected intervals of treatment could be correlated with the physical behaviour of the melt (in terms of viscosity and electrical resistivity).

SAMEVATTING

Slakke van die groep $CaO–MgO–Al_2O_3–TiO_2–SiO_2$ wat vooraf gereduseer is in grafietkroesies, is heeltemal geheroksideer om die graad en tempo van reduksie van titaanoksied te bepaal. Die invloed van slaksamestelling en temperatuur op die tempoveranderlikes is bepaal. Die graad van reduksie na gekose tydsintervalle kon in verband gebring word met die fisiese eienskappe (viskositeit en spesifieke elektriese weerstand) van die slakke.

Introduction

In an earlier paper[1] it was shown that slags belonging to the system $CaO–MgO–Al_2O_3–TiO_2–SiO_2$ undergo changes in viscosity, electrical resistivity, and melting temperature when reduced by graphite under conditions where titanium carbide or nitride is not formed. The changes in physical properties are therefore due to the removal of oxygen from the melts to a level corresponding to the lower oxides of titanium, except for highly siliceous slags from which sufficient silica is reduced to influence these properties. It is the object of this paper to discuss some of the parameters that influence the rate of reduction of the slags and to relate the physical properties to the degree of reduction. The parameters that were investigated were mainly slag composition and reduction temperature. The reducing agent was solid carbon in all cases, and the gaseous atmosphere consisted of pure argon. The electric-arc furnace operation in connection with which the research was done made the use of nitrogen instead of argon unnecessary.

Chukukere and Ross[2] reduced slags of the system $CaO–SiO_2–FeO–Al_2O_3–TiO_2$ in graphite crucibles in a nitrogen atmosphere at 1500 °C, the slag being in contact with carbon-saturated iron. They analysed the metallic phase after the titania had been reduced from the slag. For an initial titania content of 20 per cent, the reduction rate increased with CaO/SiO_2 ratio, and the replacement of nitrogen by argon did not alter the basic trend. It was also found that an increase in the titania content of the slag generally caused an increase in the rate of reduction of the oxide.

Experimental

Slag Compositions

To allow the correlation of kinetic data with the earlier results on changes in physical properties, only the small group of synthetic slags previously studied are dealt with in this paper. Table I gives the compositions of these mixtures, as well as that of a composite plant slag, HV, that was used in a determination of a realistic degree of reduction for the synthetic slags. Other experiments, performed on additional synthetic slags of the system $CaO–MgO–Al_2O_3–TiO_2–SiO_2$ and a special group containing iron and vanadium oxides as well, are reported in detail elsewhere[3].

The rate of titania reduction or the degree of reduction was studied as a function of the following composition variables:

(a) $(CaO+MgO)/SiO_2$, at constant $(TiO_2+Al_2O_3)$ and CaO/MgO ratio (series B11-B14-B17),

(b) CaO/MgO, at constant $(TiO_2+Al_2O_3)$ and basicity (series B13-B14-B15), and

(c) $(TiO_2+Al_2O_3)$, at constant CaO/MgO and basicity (series A5-B14-C23).

Reduction of Titania

The methods used in the preparation of the reduced slags are fully described elsewhere[3]. The degree of reduction that had been attained was determined by measurement of the gain in mass during complete re-oxidation of the crushed reduced slag. The re-oxidation involved maintaining the slag powder at 1100 °C in an oxygen atmosphere for 1 hour, which ensured that the oxidation of even the most severely reduced slags was complete[3].

The validity of the re-oxidation technique was assessed in a previous paper[1], and only brief comments are given here.

(a) Changes in the slag composition during reduction (as based on cation analyses) were negligible, except for the most acidic slag (B17), from which silica was noticeably reduced to SiO.

(b) Carbon was found to be present, but only in very small amounts, in the slags after they had been removed from the graphite crucible and before their viscosity and electrical resistance were determined. This carbon was not in the form of carbide.

(c) The small amount of carbon present in the as-reduced slag disappeared during the measurement

of viscosity, but this did not make a measureable difference to the gain in mass observed during re-oxidation[3].

Results and Discussion

Generally, the slags of a particular series are compared on the basis of the gain in mass during complete re-oxidation of the various members, after they had been reduced for a specified time interval at 1550 °C. Comprehensive testing on the rate of reduction, which involved testing at various reduction times, was performed only for slags B11, B14, and B17. Similarly, the effect of temperature on the rate of reduction was determined only for these three slags, and once again the emphasis was on B14.

Preliminary Work on Plant Slag HV

When the viscosity of slag HV was determined[3], it was found to be particularly low (comparable with the values reported for unreduced slags). It was therefore considered possible that it might have been reduced to a degree corresponding to the viscosity 'trough' that had been shown to exist for synthetic slags. An experiment was therefore conducted to determine an approximate state of reduction of titanium in a typical plant slag.

The magnetic fraction of slag HV was analysed for Fe, and the value obtained was assumed to represent only metallic iron. The remainder of the iron, reported as Fe_2O_3 in Table I, was assumed to be in the form of FeO. The slag was also subjected to oxidation at 1100 °C and the gain in mass recorded. It was further assumed that vanadium, manganese, and chromium are present in the reduced slag as V_2O_3, MnO, and CrO, and that both the metallic iron and the lower oxides are oxidized to the highest oxidation states of the various metals. An oxygen mass balance showed that the molar O/Ti ratio of the slag was 1,84.

Kinetic Data for Synthetic Slags

The overall reduction reaction was assumed to be

$$aTiO_2 + bC = dTi_2O_3 + fCO \quad \dots \dots \dots \dots \dots (1)$$

for the purpose of rate calculations. For (1) the rate can be expressed as

$$-dM_{TiO_2}/dt = -S/100 . dC_{TiO_2}/dt$$
$$= kA(C_{TiO_2})^a . (C_C)^b, \quad \dots \dots \dots (2)$$

where S = mass of slag (g), which was assumed constant in all cases,

$-dM_{TiO_2}/dt$ = rate of consumption of TiO_2 (g/min),

C_{TiO_2} = concentration of TiO_2 in the slag (mass %), which was calculated from the gain in mass during oxidation on the assumption that the product of reduction is Ti_2O_3,

C_C = concentration of carbon,

A = slag/carbon interfacial area (cm²) (with a slag mass of 70 g, a slag density of 3,0 g/cm³, and knowing the dimensions of the graphite crucibles, A was 38,2 cm²),

k = a rate constant.

Since the carbon concentration was constant,

$$k' = k(C_C)^b \quad \dots \dots \dots \dots \dots \dots \dots \dots (3).$$

Equation (2) could be further simplified to

$$-dC_{TiO_2}/dt = k''(C_{TiO_2})^a \quad \dots \dots \dots \dots (4)$$

and $k'' = (100k'A)/S = 54,64 \ k'$.

The order of reaction, a, was determined by the use of the logarithmic form of (4). A graph of log $(-dC_{TiO_2}/dt)$ against log C_{TiO_2} should be a straight line with slope equal to a, and the intercept of the line on the 1 per cent TiO_2 ordinate should give the value of k''. Rates were determined by the fitting of smooth curves to the experimental points of percentage TiO_2 against time and the drawing of tangents to these curves. In the single instance in which the rate could be determined at three temperatures (slag B14), an approximate value of the activation energy (E_A) could be found.

In most instances, the logarithmic plot consisted of what was taken as two straight lines. This is shown in Fig. 1 for slag B14 reduced at 1550 °C (lines AB and BC). The values of k' and a in Table II were determined from AB. The exceptions to this were slag B17 (reduced at either 1550 or 1600 °C), where only one line existed, and slag B14 (reduced at 1500 °C), where the existence of point B was doubtful. Where possible, the value of the O/Ti ratio (R) and the reduction time that correspond to point B were determined. These are given in Table II as R_B and t_B respectively. The time t_B consistently represents a reduction time at which the viscosity of a particular slag has already been increasing. The only value in the table for E_A is high and well within the range normally taken as indicative of chemical-reaction rate control. If a slag thickens appreciably, the rate of titania reduction may become dependent on the transfer of oxygen from the bulk of the slag to the reaction interface. The point B may indicate such a change in mechanism. If diffusion is to become the rate-limiting

TABLE I

COMPOSITIONS OF THE SLAGS THAT WERE STUDIED

Slag no.	(CaO+MgO)/SiO₂	Mass per cent				
		TiO₂	Al₂O₃	SiO₂	CaO	MgO
A5	1,401	24,800	11,200	26,650	18,675	18,675
B11	1,699	30,200	13,800	20,750	17,625	17,625
B13	1,400	30,200	13,800	23,330	21,780	10,890
B14	1,400	30,200	13,800	23,330	16,335	16,335
B15	1,400	30,200	13,800	23,330	10,890	21,780
B17	0,801	30,200	13,800	31,100	12,450	12,450
C23	1,397	37,180	16,820	19,190	13,405	13,405
HV*	1,530	30,94	13,04	20,32	14,64	16,43

*The other constituents of HV are as follows in mass per cent: V_2O_5 0,73, Mn_3O_4 0,72, Cr_2O_3 0,18, and Fe_2O_3 3,76.

step, a treatment of the data as outlined below suggests itself.

Still referring to reaction (1),

$$-dC_{TiO_2}/dt = D_{TiO_2} \cdot A/\delta [C_{TiO_2}(i) - C_{TiO_2}(b)], \quad . \quad . \quad (5)$$

where

D_{TiO_2} = diffusivity of TiO_2 in the slag,

A = interfacial area,

δ = effective thickness of the boundary layer at the slag-graphite interface,

$C_{TiO_2}(i)$ = concentration of TiO_2 at the interface,

$C_{TiO_2}(b)$ = bulk concentration of TiO_2.

If $C_{TiO_2}(i)$ is assumed to be negligible, equation (5) becomes

$$dC_{TiO_2}/dt = D_{TiO_2} \cdot A/\delta \, (C_{TiO_2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

The diffusion boundary layer will be of constant thickness (δ) only if there is no evolution of gas. In the present system, this condition is not fulfilled. On the contrary, the rate of agitation of the melt by bubbles of carbon monoxide and silicon monoxide will be a function of the reduction rates of both silica and titania. If it were possible to assume that δ was a function only of dC_{TiO_2}/dt, Wagner's[4] empirical relation might have been useful:

$$\delta = j[dC_{TiO_2}/A\,dt]^{-\beta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .(7)$$

where j and β are constants.

Substitution of (7) into (6) gives

$$dC_{TiO_2}/dt = A^{1-\beta}[D_{TiO_2} \cdot C_{TiO_2}/j]^{1/(1-\beta)}. \quad . \quad . \quad . \quad (8)$$

An approximate value of the order of reaction might be obtained from the kinetic data. Substitution into (8) would give a value of β, and the apparent rate constant
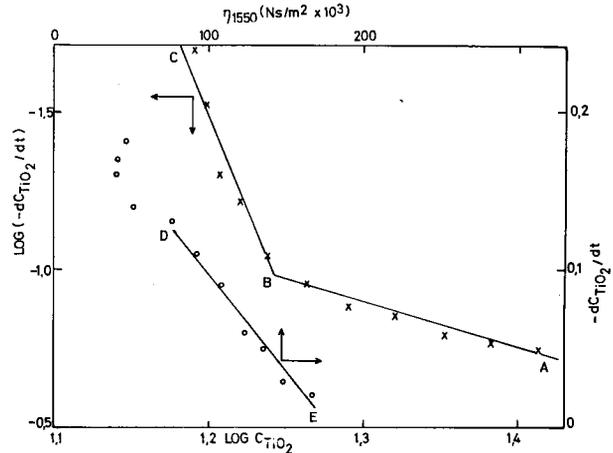

Fig. 1—Order of reaction and rate constant for slag B14 (reduced at 1550°C) and the rate–viscosity relationship

TABLE II

REDUCING CHARACTERISTICS OF SYNTHETIC TITANIFEROUS SLAGS

Slag no.	Reduction temp. °C	Reduction time min	Mass gain in oxidation %	Molar O/Ti	C_{TiO_2} mass %	k' $\times 10^5$	a	E_A	t_B min	R_B	t_D min	R_D	$\eta - \eta_0$
A5	1550	60	0,893	1,82	15,9								+
B11	1550	0	0,283	1,95	27,4								
		30	0,940	1,84	20,8								—
		60	1,350	1,78	16,7								+
		90	1,500	1,75	15,2								
		120	1,610	1,73	14,1	7,65	1,2		72	1,76	45	1,81	+
	1600	30	1,139	1,81	18,8								+
		60	1,750	1,72	12,7								+
		90	2,040	1,66	9,8								
		120	2,130	1,64	8,9	31,1	0,9		60	1,71			
B13	1550	60	0,966	1,84	20,5								+
B14	1500	0	0,240	1,96	27,8								
		30	0,520	1,91	25,0								—
		60	0,892	1,85	21,3								
		90	1,090	1,82	19,3	2,15	1,4						+
	1550	30	0,789	1,87	22,6								—
		60	1,163	1,81	18,6								+
		90	1,384	1,77	16,4								+
		120	1,466	1,76	15,5	4,09	1,3	448	70	1,79	46	1,82	
	1600	20	0,890	1,85	21,3								+
		30	1,010	1,83	20,1								+
		45	1,354	1,78	16,7								+
		90	1,916	1,68	11,4								
		120	2,130	1,64	8,9	10,5	1,3		69	1,71	55	1,74	
B15	1550	60	1,287	1,79	17,3								+
B17	1550	0	0,210	1,97	28,1								
		30	0,600	1,90	24,2								—
		60	0,980	1,84	20,4								—
		90	1,287	1,79	17,3								—
		120	1,450	1,76	15,7	2,59	1,4						—
	1600	20	0,600	1,90	24,2								—
		60	1,200	1,80	18,2								—
		90	1,614	1,73	14,1	10,1	1,1						
C23	1550	60	2,677	1,64	10,4								+

Underlining indicates the ratio of slags that were reduced at 1550°C for 60 min.

E_A is expressed in kJ/mol . K

would be expressed in terms of A, D_{TiO_2}, and j. However, D_{TiO_2} is not a constant either, but, according to Yavoyskiy[5], is related to viscosity through the relationship

$$D_{TiO_2} = const/\eta. \qquad \ldots \ldots \ldots \ldots \ldots \ldots (9)$$

Accordingly, a relationship was sought between the apparent rate of titania reduction and the viscosity at the reduction temperature. For slags B11 and B14, reduced at 1550° and 1600 °C for longer times, the relationship was found to be linear. The line ED in Fig. 1 serves as an example. Again, the O/Ti ratio and the time corresponding to point D were calculated. These are given as R_D and t_D in Table II. Again, slag B17 is an exception in that there is negligible correlation between the rate of reduction and the viscosity.

Rate of Oxygen Loss

In Table II, the molar O/Ti ratios of slags that were reduced at 1550° for 60 minutes are underlined. The parameter R_{1550}^{60} will be generally used to compare the reducing behaviour of different slags.

As the mass basicity ratio, $(CaO+MgO)/SiO_2$, was increased from 0,8 (B17) through 1,4 (B14) to 1,7 (B11), R_{1550}^{60} decreased from 1,84 through 1,81 to 1,78. The corresponding increase in the rate constant k' is from $2,59 \times 10^{-5}$ through $4,09 \times 10^{-5}$ to $7,65 \times 10^{-5}$. This trend is in agreement with the findings of Chukukere and Ross[2]. At a reduction temperature of 1600 °C, the trend is still recognizable, but there is little difference between the values of k' for slags B14 and B17. This is probably due to the fact that the loss of silica (as SiO) from B17 (the most acidic slag) caused its composition to approach that of the more basic B14.

The effect of the mass ratio CaO/MgO on the rate of removal of oxygen from the slag is illustrated by Fig. 2. Higher magnesia contents appear to cause slightly faster rates of reduction of titania. It must also be pointed out that the three slags B13, B14, and B15 possess molar $(CaO+MgO)/SiO_2$ ratios of 1,70, 1,78 and 1,91 respectively, so that the line in Fig. 2 can equally well be referred to the linear upper scale of molar basicity ratio. This points to the possibility that replacement of CaO by MgO on a molar basis at constant molar basicity ratio may in fact have very little influence on the rate of reduction.

The influence of the $(TiO_2+Al_2O_3)$ concentration can also be assessed in terms of R_{1550}^{60} (slags A5, B14 and C23). An increase in $(TiO_2+Al_2O_3)$ from 44 to 54 per cent had a more pronounced effect on the O/Ti ratio than any of the other composition variables over the ranges that were tested.

The effect of an increase in the reduction temperature as one of accelerating the rate of oxygen removal from any particular slag is clearly shown in Table II.

The lines in Fig. 1 strongly suggest a transition from chemical-reaction rate control to diffusion rate control due to the thickening of the slag. Considering both R_B and R_D, this transition appears to take place in the range of O/Ti values between 1,74 and 1,79. This means

that the reduction reaction will become self-inhibiting when a slag has been reduced to an O/Ti ratio lower than this.

Degree of Reduction and Viscosity

It was pointed out previously that, with the exception of B17, the viscosity of the slag tends to pass through a minimum and to increase thereafter upon further reduction. In Table II, $\eta-\eta_0$ is the algebraic sign of the difference between the viscosity of a reduced slag and that of the unreduced master slag at the same temperature. The indications are that the viscosity minimum corresponds to an O/Ti ratio of approximately 1,84. (B17 is an exception because of the appreciable removal of silica from the melt during reduction.) It follows, then, that a change in any variable that increases the rate of oxygen removal will also cause more-basic slags to thicken faster. These changes have been shown to be an increase in basicity, MgO/CaO ratio, $(TiO_2+Al_2O_3)$ concentration, or temperature.

As already mentioned, the O/Ti ratio of the plant slag, HV, was found to be 1,84. Such a slag is not ex-
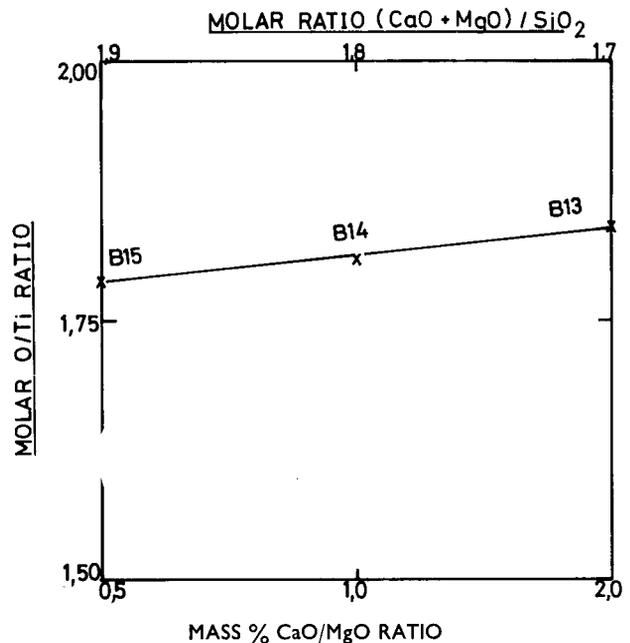

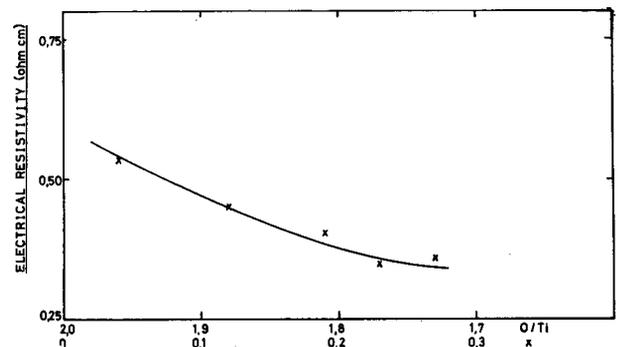Fig. 2—The effect of CaO/MgO ratio on reduction (60 min at 1550°C)

Fig. 3—Relationship between degree of reduction and resistivity of slag B14 at 1550°C

pected to have undergone a viscosity increase, as was confirmed by the viscosity measurement. Iron oxide, which was present in HV but not in the synthetic slags, acts mainly in two ways during the reduction of a titaniferous melt:

(a) it screens TiO_2 from reduction much more effectively than SiO_2 does, and

(b) residual FeO provides oxygen ions to the melt, which must serve to lower the viscosity.

Reducing Conditions and Electrical Resistivity

Measurements of electrical resistance were carried out on the full range of reduced derivatives of slag B14. Fig. 3 is a graph of resistivity against the molar O/Ti ratio or the quantity $x = (2 - O/Ti)$. The curve that was fitted to the experimental points is the quadratic

$$\rho_{1550} = 2,32\ x^2 - 1,54\ x + 0,59,$$

but there is little experimental evidence for an increase in the resistivity at values of x greater than that corresponding to the minimum of the function. This approach is based on that of Engell and Vygen[6], who assumed that the contribution of electronic conduction in siliceous slags containing iron oxide must be given by $bx(1-x)$, where $x = Fe^{3+}/Fe$, as the number of Fe^{3+} nearest neighbour to an Fe^{2+} ion is proportional to $x(1-x)$. Such a function has a maximum where $x = 0,5$, which is

in accord with what is known of the particular system. If x also has an influence on ionic conduction, this simple model breaks down.

The function suggested above has a projected minimum at $x = 0,33$, a value that corresponds to the stoichiometry of Ti_3O_5. This indicates a maximum electronic-conduction contribution between Ti^{3+} and Ti^{4+}. The viscosity data on the same slag (B14) indicate a complex indirect dependence of ionic conduction on x. Unless ionic conduction is more severely influenced by carriers other than titanium ions, the association of $x = 0,33$ with electronic conduction remains speculative.

References

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Project management

The colloquium 'Project management in the metallurgical industry' will be held during September 1980, and not during March 1980 as indicated in the original call for papers. Intending authors are asked to note the change and to submit proposed titles for papers before September 1979 to the Secretary, South African Institute of Mining and Metallurgy, P.O. Box 61019, Marshalltown, 2107.

Emission spectroscopy

The National Institute for Metallurgy, the South African Chemical Institute (Southern Transvaal Section), and the Spectroscopic Society of South Africa are arranging a symposium that will review recent developments in emission spectroscopy with special reference to inductively coupled plasmas. The meeting, entitled the Symposium on Recent Developments in Emission Spectroscopy, is to be held at the National Institute for Metallurgy, Randburg, on 17th and 18th April, 1980.

Over the years, there has been a considerable upsurge of interest in inductively coupled plasma (I.C.P.) as an excitation source for emission spectroscopy, and in its application to a wide variety of analytical problems in geochemistry, metallurgy, environmental pollution, biological analysis, and other fields. The original investigators made claims of high activity and freedom from interference, and these claims have been substantiated to a large extent. As a technique, it is generally unknown to a large section of potential users. It could be of great value to many mining and industrial organizations, which are, as yet, not fully acquainted with its capabilities. These organizations are unaware that it could be applied successfully to their particular analytical problems.

This Symposium aims to show potential users the

extent of its value and to bring this technique and it applications to the notice of all interested parties in South Africa. The main speaker will be a world authority on this technique.

Other excitation techniques, such as those using glow discharge, high-repetition-rate spark, and argon-jet spark, will be dealt with in the other sessions. There will be demonstrations of equipment during the Symposium.

Contributions, in English only, concerning any of those areas are invited. Titles of contributions, with short abstracts (100 words), should be submitted by 1st October, 1979. Authors will not be expected to submit full-length papers, but extended abstracts, which will be distributed to all the delegates, must be submitted before 15th January, 1980.

The proceedings of the Symposium will not be published, and authors wishing to have papers published are free, after the Symposium, to submit them to any journals of their choice.

All communications should be addressed to The Head, Liaison & Information Division, National Institute for Metallurgy, Private Bag X3015, Randburg, 2125 South Africa.