SOLID ELECTROLYTES AND DEOXIDATION

SOLID ELECTROLYTES AND DEOXIDATION

By

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A study has been made of the transformation of deoxidation products in the Fe-V-O system in the temperature range 1545 - 1640°C, using galvanic cells with solid electrolytes. The cells used were in the form of $2rO_2$ (CaO) immersion probes and $ThO_2(Y_2O_3)$ crucible assemblies. The fields of study of FeV_2O_4 (spinel) and V_2O_3 were established with respect to oxygen activity and temperature.

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INTRODUCTION

The solubility of oxygen in pure liquid iron is 0.16 w/0 at the melting temperature. On solidification this decreases to a very low level; in γ -iron it is estimated as about 0.003 w/0 ⁽⁶⁴⁾. In liquid steel the amount of oxygen in solution is lowered by the presence of the other solute elements, and the actual concentration is usually between these two limits ⁽⁶⁴⁾, but when the metal solidifies the excess of oxygen is rejected from solution and combines with the other elements to form oxides. When this excess oxygen combines with carbon to form CO according to the following equation

$$[C]_{1w+2} + [O]_{1w+2} = CO(g)$$
(1.1)

most of this carbon monoxide escapes as gas but some bubbles remain trapped by the solidified metal.

In rimming and semi-killed steels, controlled CO evolution is used to balance volume shrinkage due to solidification. In killed steel CO evolution must be eliminated. The control or elimination of CO evolution can be accomplished by the addition of deoxidants which form

oxides of greater stability than carbon monoxide. Deoxidants are added prior to solidification such that the oxide deoxidation products are removed by flotation. The elements commonly used are manganese, silicon, aluminum, vanadium, chromium, etc.

The deoxidizing power of an element in liquid steel depends upon its activity, its effect on the activity coefficient of oxygen, and also on the free energy of formation and the nature of the deoxidation product.

When a deoxidant is added to the bath, a reaction occurs in which dissolved oxygen is removed from solution in the metal, forming the oxide of the deoxidant. The reaction ceases when equilibrium is reached; that is when the oxygen activity is reduced to a definite value described by the equilibrium constant. The equations for the reaction and its equilibrium constant are:

$$[M]_{1wt} + [O]_{1wt} = MO ; K = \frac{a_{MO}}{a_{M} \times a_{O}}$$
(1.2)

In cases in which the oxide MO appears as a pure solid, or liquid it follows that:

$$[M] \times [O] = K^{1}$$
 (1.3)

where K' is the deoxidation constant.

Most of the oxide products that form during this deoxidation float to the surface of the solidifying casting, but some may become entrapped and remain within the metal as inclusions. Apart from the detrimental effect of nonmetallic inclusions on the mechanical properties of a metal, particularly fatigue life, some of the oxides are semi-molten at hot-working temperatures forming grain boundary films which can give rise to poor ductility and hot shortness during fabrication (64).

It has been shown (1,2,13) that some of the deoxidants, such as Al, V and Cr, form different oxides that have different separation tendencies from the liquid steel. These oxides are FeO.M₂O_x, which are called spinel, and M₂O_x. While the latter oxide separates readily from the liquid steel, the former, spinel, has a lower interfacial tension and thus a lower separation tendency.

At high oxygen activities, the spinel is the deoxidation product, whereas at low oxygen activities the $M_2^{0}x$ oxide is formed. At a constant temperature, it follows that at one particular oxygen activity, Fe0.M₂⁰x and M₂⁰x coexist together in simultaneous equilibrium with oxygen.

In order to obtain a clean steel, the deoxidation should be carried out such that M_2O_x is the deoxidation product. Hence, it is important to determine that particular oxygen activity at which the transition of one type of oxide to the other occurs. The relative ease and reliability of the galvanic cell technique, incorporating a solid (oxide) electrolyte, for the determination of the oxygen activity of a melt, has made it of particular interest to metallurgists. During the last few years, this electromotive force (EMF) method has been extensively used to determine the thermodynamic behaviour of oxygen at steelmaking temperatures.

In this work, an investigation has been carried out to establish a direct method of determining the transition oxygen activity in Fe-V-O system, at which FeO.V₂O₃ transforms to V₂O₃. This was accomplished by the use of "oxygen probes", and a galvanic cell, specially designed to monitor, continuously, the behaviour of oxygen in Fe-V-O melts, in the temperature range of 1550-1650°C. A series of EMF measurements with time were carried out during the oxidation and/or deoxidation of Fe-V-O melts with the cell arrangement:

Since the oxygen content of the melt is directly related to the measured EMF, these high temperature titrations were used to construct deoxidation diagrams for the Fe-V-O system.

The solid electrolytes employed were ZrO₂(CaO), Calcia Stabilized Zirconia (CSZ) and ThO₂(Y₂O₃), Yttria Doped Thoria (YDT). The YDT was manufactured by a slip casting method, in the form of small crucibles.

GALVANIC CELLS USING SOLID OXIDE ELECTROLYTE

2.1. INTRODUCTION

Galvanic concentration cells using solid oxide electrolytes have been chosen in this investigation to study the thermodynamic equilibria in the Fe-V-O system at steelmaking temperatures.

This technique has proved to be successful in a large number of cases (8,13,17), and is finding growing applications in industry (19,35).

In the following sections, the principles and limitations of these techniques will be described.

2.2. THE OXYGEN CONCENTRATION CELL

Essentially a galvanic cell is formed by separating the components of a chemical reaction by a chemically inert electrolyte, which ideally offers transport for one charged species only.

Specifically, an oxygen concentration cell consists of two electrodes with oxygen chemical potential μ_1 and μ_2 which are separated by a solid oxide electrolyte that conducts essentially via oxygen ions ⁽³⁾.

Such a cell may be represented as

Pt
$$| \mu_{(O_2)}^{I} |$$
 solid oxide $| \mu_{(O_2)}^{II} |$ Pt (II)

with a cell reaction

$$O_2(\mu_{II}) = O_2(\mu_{I})$$
 (2.1)

At elevated temperatures (>500°C) a potential difference develops across this cell which is a source of an electromotive force (EMF), $E^{(3)}$. The Gibbs free energy change, ΔG , for the cell reactions, which occurs when n Faradays are transferred from the cathode to the anode, is

$$\Delta G = \mu_{(O_2)}^{II} - \mu_{(O_2)}^{I} \quad [cal.-mole^{-1}]$$

= -nEF (2.2)

where n denotes the number of Faradays to be passed across the cell in order to affect the reaction under consideration, F is Faraday's constant and μ_{I} and μ_{II} are the chemical potentials at the right and left electrodes respectively.

Equation (2.2) requires that the solid electrolyte be a purely ionic conductor. While electronic conduction in aqueous electrolytes is always negligible, crystalline compounds exhibit partial electronic conductivities that are rarely negligible ⁽⁵⁾. In such cases the relation between the cell EMF and ΔG stated in Eq. (2.2) must be replaced by another relationship.

According to Wagner ⁽³⁾, the EMF of a galvanic cell based on an electrolyte which exhibits only slight deviation from the ideal stoichiometry, is given by the expression:

$$E = \frac{1}{2ZF} \int_{\mu_{(0_2)}}^{\mu_{(0_2)}} t_{ion} d\mu_{(0_2)}$$
(2.3)

where Z is the absolute value of the valence of oxygen, and t_{ion} is the transport number for the oxygen ion in the electrolyte. Since $t_{ion} + t_e = 1$, where t_e is the transport number for electrons, one may write ⁽³⁾

$$E = \frac{1}{2ZF} \int_{\mu}^{\mu} \frac{[0]_{(0_2)}^{(0_2)}}{[0]_{(0_2)}^{(1-t_e)d\mu}} (0_2)$$

= $\frac{\mu_{(0_2)}^{(0_2)} - \mu_{(0_2)}^{(1)}}{2ZF} - \frac{1}{2ZF} \int_{\mu_{(0_2)}^{(1-t_e)}}^{\mu_{(0_2)}^{(1-t_e)}} t_e d\mu_{(0_2)}$ (2.4)

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From Eqs. (2.4) and (2.2) it follows that

$$\Delta G = -2ZFE - \int_{\mu_{(0_2)}}^{\mu_{(0_2)}} t_e d\mu_{(0_2)}$$
(2.5)

where the second term on the right hand side is a correction term of the solid electrolyte that is predominantly an ionic conductor, i.e., t_e is much smaller than unity ⁽³⁾.

2.2.1. Performance Characteristics of Oxygen Cells Under Steady State Conditions

Consider a solid electrolyte with mixed conduction which is in contact with two electrodes with fixed oxygen chemical potentials. Figures 2.1 and 2.2 schematically represent the physical system and its equivalent electrical circuit corresponding to the above situation.

According to Choudhury and Patterson ⁽⁶⁰⁾, under a completely reversible condition, if the source in Fig. 2.2 is a load resistor of infinite impedance, or a battery with



Fig. 2.1



Fig. 2.2 Linear circuit analog for a solid electrolyte oxygen concentration cell

an appropriate bucking EMF, I_{ext} . vanishes, and the electrolyte is said to be functioning in the open circuit mode. Inspection of the circuit diagram in Fig. 2.2 indicates that neither I_{ion} nor I_e vanishes in the open circuit case but rather $I_{ion} = -I_e$.

If the source in Fig. 2.2 is a battery with the same polarity and EMF as $E_{Th} = [\mu_{(O_2)}^{I} - \mu_{(O_2)}^{II}]/2ZF$, I vanishes and $I_{ext.} = I_e$ only ^(60,61). In this case one may write ⁽⁶⁰⁾

$$V_{\rm T} = \frac{1}{22F} \int_{\mu^{\rm I}(O_2)}^{\mu^{\rm II}(O_2)} d\mu_{(O_2)} \qquad (2.6)$$

This technique can be used in "potentiostatic" experiments with a cell of the type

$$p'_{0_2}(air) | solid electrolyte | a''_{0} in Fe(l) | . (III)$$

When the cell III is subjected to an applied voltage, $E_{appl.}$, the ionic current will vanish at steady state. As a consequence the steady-state chemical potential for oxygen in liquid metal is given by ⁽⁶¹⁾

$$E_{appl.}(I_{ion}=0) = \frac{RT}{4F} \ln \frac{p_{O_2}^{*}}{p_{O_2}^{*}}$$
 (2.7)

and at any time before the steady-state is given by (61,62)

$$E_{appl.} - I_{ion}(t)\Omega_{ion} = \frac{RT}{4F} \ln \frac{p_{O_2}^{"}}{p_{O_2}(t)}$$
 (2.8)

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where Ω_{ion} is the ionic resistance.

If the source battery polarity remains the same but its EMF is increased, the cell is said to be in the charging mode (60).

If the source voltage is less than the voltage expressed by Eq. (2.3) (§2.2) the cell is said to be discharging under load ⁽⁶⁰⁾. By inspections of Fig. 2.2 it is seen that I_{ion} and I_{e} will flow in opposite directions.

2.3. MEASUREMENTS OF TRANSPORT NUMBERS FROM CELL EMF

METHOD A: If the total conductivity (σ_{T}) of the electrolyte is represented as the sum of the ionic (σ_{ion}) and electronic (σ_{c}) conductivities, i.e.,

$$\sigma_{\rm T} = \sigma_{\rm ion} + \sigma_{\rm e} = \sigma_{\rm ion} + \sigma_{\oplus} + \sigma_{\Theta}$$
(2.9)

where σ_{\oplus} is the conductivity due to positive hole conduction (p-type semiconduction) and σ_{\oplus} is the electronic conductivity due to excess electron conduction (n-type semiconduction), we can define the transport number of any charge carrying species as the fraction of the total conductivity due to these species ⁽⁷⁾. The transport number, t_{ion} , for ions will then be

$$t_{ion} = \frac{\sigma_{ion}}{\sigma_{T}} = \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_{e}}$$
(2.10)

which can be measured using a null current potentiometer ⁽⁷⁾.

Following the analysis of Mitoff ⁽⁷⁾ one may apply the Kirchoff's law to Fig. 2.2, when the system is under open circuit condition, i.e., when the source in Fig. 2.2 is replaced by a null current potentiometer which measures the voltage difference, E_p . Thus

$$I_{ext.} = I_{ion} + I_e = 0$$
 (2.11)

$$E_{p} = E_{Th} + I_{ion} \left(\frac{\ell}{A\sigma_{ion}}\right)$$
(2.12)

$$E_{p} = I_{e} \left(\frac{\ell}{A\sigma_{e}}\right)$$
(2.13)

where $I_{ext.}$, I_{ion} and I_e are external current, ionic current and electronic current respectively, and (l/A) is the electrolyte thickness-area ratio.

Using Eqs. (2.11), (2.12) and (2.13) one may write

$$E_{p}\sigma_{e}(\frac{A}{\hat{k}}) = E_{Th}(\frac{A}{\hat{k}})(\frac{\sigma_{e}\sigma_{ion}}{\sigma_{e}+\sigma_{ion}})$$
(2.14)

or

$$\frac{E_{p}}{E_{Th}} = \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_{e}} = \frac{\sigma_{ion}}{\sigma_{T}} = t_{ion} . \qquad (2.15)$$

Inspection of Eqs. (2.15) and (2.4) indicates that the occurance of any electronic conduction will reduce the theoretical EMF, i.e., E_{Th} . If the charge is carried exclusively by ions, E_p will be equal to E_{Th} ($\sigma_e << \sigma_{ion}$). If the charge is carried by electrons, σ_e will short out E_{Th} and then $E_p = 0$ ⁽⁷⁾.

METHOD B: This method is based on the defect structure and the characteristic changes in conductivities of solid electrolytes under conditions of varying oxygen partial pressure ⁽⁴⁾. Presumably the p_{0_2} dependence of the excess electron conductivity σ_{Θ} and the positive hole conductivity σ_{Θ} are dictated by the local equilibria ⁽⁴⁾

$$\frac{1}{2} O_2(g) + V_0^{"} + 2\Theta = O_{OX}$$
(2.16)

and

$$\frac{1}{2} O_2(g) + V_{O} = 2\Theta + O_{O^{\mathbf{X}}}$$
(2.17)

where 0_{OX} is an oxygen ion in its lattice site, V_{O} is a vacant oxygen ion site, and \oplus and Θ denote a positive hole and an excess electron, respectively. If the abundant dopant cations and the compensating oppositely charged anion vacancies are sufficiently dissociated, these species should satisfy the neutrality condition (8)

$$\sum_{i=1}^{S} C_{i}q_{i} = 0$$
(2.18)

with

or

$$[V_{O}] = [Ca_{Zr''}]$$
 for CSZ (2.19)

 $[V_{\ddot{O}}] = \frac{1}{2} [Y_{\rm Th}]$ for YDT (2.20)

where C_i is concentration (particle-cm⁻³), q_i is the charge (Coulombs-particle⁻¹), $[V_{\ddot{O}}]$, $[Ca_{Zr}"]$ and $[Y_{Th}]$ represent the concentrations of the fully ionized, dissociated species ⁽⁸⁾. At a given temperature, $[V_{\ddot{O}}]$ should be established by the dopant content and, therefore, changes only slightly with P_{O_2} , so that the equilibrium constants for Eqs. (2.16) and (2.17) give C_{Θ} to be proportional to $p_{O_2}^{-1/4}$ and C_{\oplus} proportional to $p_{O_2}^{1/4}$, if a dilute solution of electronic defect is assumed ⁽⁴⁾. These same dependencies extend immediately to σ_{Θ} and σ_{\oplus} , respectively, through the relation ⁽⁸⁾

$$\sigma_{T} = \sum_{i=1}^{S} q_{i}^{2} C_{i} B_{i} = \sum_{i=1}^{S} \sigma_{i}$$
(2.21)

where σ_{T} = total conductivity of a material containing S independently migrating species.

> B_i = the absolute mobility (particle-cm²-sec⁻¹-volt⁻¹ -Coulombs⁻¹)

 σ_i = partial conductivity of the i species.

This necessitates that B_i be independent of C_{Θ} and C_{Θ} ⁽⁸⁾.

Assuming the above conditions, it follows that the total conductivity is related to the oxygen partial pressure as follows:

$$\sigma_{\rm T} = \sigma_{\rm ion} + k_1 p_0^{+1/4} + k_2 p_0^{-1/4}$$
(2.22)

for the system of CSZ and YDT (8). A more general form of Eq. (2.22) is

$$\sigma_{\rm T} = \sigma_{\rm ion} + k_1 p_0^{1/n} + k_2 p_0^{-1/m} \qquad (2.23)$$

The values of n and m depend on the type of defects predominating over a given range of oxygen pressures ⁽⁹⁾. Thus, if the total conductivity is a function of oxygen partial pressure, this implies an electronic contribution, and the ionic transference number, t_{ion} , will not be unity.

Figure 2.3 schematically shows the variation of total conductivity of oxides as a function of oxygen partial pressure.

Once the total conductivity relationship is determined, for a given solid electrolyte, one may obtain the ionic transport number by combining Eqs. (2.10) and (2.23):

$$t_{ion} = \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_{\oplus} + \sigma_{\Theta}} = (1 + k_1 p_{0_2}^{1/n} + k_2 p_{0_2}^{-1/m})^{-1} (2.24)$$

where k_1 , k_2 , n and m are constants. The values of k_1 and k_2 depend on the dopant concentration and temperature ⁽⁸⁾. The key factors in determining k_1 and k_2 are the points A and B in Fig. 2.3, at which $\sigma_{ion} = \sigma_{\Theta}$ and $\sigma_{ion} = \sigma_{\Theta}$ at low and high oxygen partial pressures, respectively.

To find k_1 , consider point A at which $\sigma_{ion} = \sigma_{\Theta}$ and $t_{ion} = 0.5$. If the pressure corresponding to this point is called p_{α} , then

$$0.5 = [1 + k_1 p_{\oplus}^{1/n}]^{-1}$$

Solving for k, one obtains

16

(2.25)

Fig. 2.3 Schematic representation of the variations of total conductivity with oxygen partial pressure

という

1.15



LOG P_{O2} + (b)

$$k_1 = (1/p_{\oplus})^{1/n}$$
 (2.26)

The same way

$$k_2 = (1/p_{\Theta})^{-1/m}$$
 (2.27)

where p_{Θ} is the oxygen pressure corresponding to the point B, at which $\sigma_{ion} = \sigma_{\Theta}$.

Upon substitution of Eqs. (2.26) and (2.27) into Eq. (2.24), the ionic transport number will be given by:

$$t_{ion} = [1 + (\frac{p_{02}}{p_{\oplus}})^{1/n} + (\frac{p_{02}}{p_{\oplus}})^{-1/m}]^{-1}$$
(2.28)

as shown by Schmalzeried (5,9). In Eq. (2.28) p_{\oplus} , p_{Θ} , n and m are constants.

Considering cell II,

Pt
$$O_2(p_{O_2}^{"})$$
 solid electrolyte $O_2(p_{O_2}^{"})$ Pt (II)

where the $p_{0_2}^{"}$ is the reference electrode at high $p_{0_2}^{~}$ and p' is the electrode of variable, low $p_{0_2}^{~}$. Schmalzeried (71) substituted Eq. (2.28) into Eq. (2.3) and changed the chemical potentials to partial pressures, to obtain

$$E = \frac{RT}{ZF} \int_{p_{0_2}^{"}}^{p_{0_2}^{'}} [1 + (\frac{p_{0_2}}{p_{\oplus}})^{1/n} + (\frac{p_{0_2}}{p_{\Theta}})^{-1/n}]^{-1} dp_{0_2}/p_{0_2}(2.29)$$

and integrating he obtained

$$E = \frac{RT}{ZF} \left[\ln \left(\frac{p_{\oplus}^{1/n} + p_{O}^{1/n}}{p_{\oplus}^{1/n} + p_{O}^{n}} + \ln \left(\frac{p_{\Theta}^{1/n} + p_{O}^{n}}{p_{\Theta}^{1/n} + p_{O}^{n}} \right) \right]$$
(2.30)

where n is set to be equal to m. Obviously Eq. (2.30) reduces to the theoretical cell voltage with $t_{ion} = 1$, when $p_{\Theta} << p_{O_2}' < p_{\Theta_2}' << p_{\oplus}$, i.e., $E = \frac{RT}{ZF} \ln(\frac{p_{O_2}'}{p_{O_2}'})$ (2.31)

which is a modification of Eq. (2.2).

2.3.1. Extrapolation of Conductivity Diagram to Higher Temperatures

Determination of high temperature ionic transport number and/or conductivities from low temperature data is only possible if a complete and reliable knowledge of conductivities as a function of temperature are available.

At constant p_{0_2} , all three conductivity modes exhibit an Arrhenius type temperature dependence with apparent activation energies Q_{ion} , Q_{Θ} , Q_{Θ} that are also p_{0_2} and temperature independent.

In view of these considerations it is possible to characterize the conductivities σ_{ion} , σ_{Θ} and σ_{Θ} as

$$\sigma_{\rm T} = \sigma_{\rm ion} + \sigma_{\rm \Theta} + \sigma_{\rm \Theta} \tag{2.9}$$

where

$$\sigma_{\text{ion}} = \sigma_{\text{ion}}^{\circ} \exp(-Q_{\text{ion}}/RT)$$
 (2.32)

$$\sigma_{\oplus} = \sigma_{\oplus}^{\circ} p_{O_2}^{1/n} \exp(-Q_{\oplus}/RT)$$
(2.33)

$$\sigma_{\Theta} = \sigma_{\Theta}^{\circ} p_{O_2}^{-1/n} \exp(-Q_{\Theta}/RT)$$
 (2.34)

and where the quantities σ_{\oplus}° , σ_{Θ}° , n, Q_{ion} , Q_{\oplus} , and Q_{Θ} are all $P_{O_2}^{\circ}$ - and T-independent ⁽¹⁰⁾. The boundaries of the ionic domain may be deduced by equating σ_{\oplus} and σ_{Θ} to σ_{ion} and taking the logarithm of the results. Thus at high $P_{O_2}^{\circ}$; $\sigma_{\text{ion}} = \sigma_{\oplus}^{\circ}$ which gives

$$\log p_{\oplus} = -n \left(\frac{Q_{ion} - Q_{\oplus}}{2.303 \text{ R}}\right) \frac{1}{T} + n \log \frac{\sigma_{ion}}{\sigma_{\oplus}^{0}}$$
(2.35)

and at low p_{0_2} ; $\sigma_{ion} = \sigma_{\theta}$ which gives

$$\log p_{\Theta} = +n \left(\frac{Q_{\text{ion}} - Q_{\Theta}}{2.303 \text{ R}}\right) \frac{1}{T} - n \log \frac{\sigma_{\text{ion}}^{\bullet}}{\sigma_{\Theta}^{0}}$$
(2.36)

If log p_{O_2} is plotted against 1/T, Eqs. (2.35) and (2.36) will be straight lines of the form

$$\log p = m(\frac{1}{T}) + B$$
, (2.37)

where $m = -n[(Q_{ion} - Q_{\oplus})/2.303 \text{ R}]$ for log p_{\oplus} relation and $m = +n[(Q_{ion} - Q_{\oplus})/2.303 \text{ R}]$ for log p_{Θ} relation and the intercepts are $n \log(\sigma_{ion}^{\circ}/\sigma_{\oplus}^{\circ})$ and $n \log(\sigma_{ion}^{\circ}/\sigma_{\Theta}^{\circ})$ corresponding to Eqs. (2.35) and (2.36) respectively.

These lines could be imagined to be the projection of a three dimensional log $\sigma_{\rm T}$, log ${\rm p}_{0_2}$, l/T space onto the log ${\rm p}_{0_2}$, l/T plane ^(10,11). If the electrolytic domain is defined by the condition that $\sigma_{\rm ion}$ is simply greater than either σ_{Θ} or σ_{\oplus} , i.e., $t_{\rm ion} \ge 0.5$, one may find the electrolytic boundaries from the locus of log ${\rm p}_{\oplus}$ or log ${\rm p}_{\Theta}$, l/T points by equating $\sigma_{\rm ion}$ to 100 σ_{\oplus} and 100 σ_{Θ} ⁽¹¹⁾. In log ${\rm p}_{0_2}$, l/T space solution of Eqs. (2.35) and (2.36) with the above conditions gives the following equations for the electrolytic domain boundaries:

$$\log p_{0_{2}} = -n \left(\frac{2 \operatorname{ion} - 2_{\oplus}}{2 \cdot 303 \operatorname{R}}\right) \frac{1}{\operatorname{T}} + n \log \frac{\sigma_{\operatorname{ion}}^{\circ}}{100 \sigma_{\oplus}^{\circ}}$$
$$= \log p_{\oplus} - 2n \qquad (2.38)$$

and

$$\log p_{0_2} = +n \left(\frac{Q_{10n} - Q_{\Theta}}{2.303 \text{ R}}\right) \frac{1}{T} - n \log \frac{\sigma_{10n}^{\circ}}{100 \sigma_{\Theta}^{\circ}}$$
$$= \log p_{\Theta} + 2n \quad .$$

These boundaries are critical in the evaluation of a given mixed conductor for use as a solid electrolyte. Any application requiring electrolytic behaviour must correspond

(2.39)

to log P_{0_2} , 1/T conditions which lie between the lines corresponding to Eqs. (2.38) and (2.39). It is important to note that these lines may be extrapolated even if direct measurements have established their positions only over limited ranges of P_{0_2} and T ⁽¹¹⁾. Such extrapolations are justified over ranges where the parameters Q_{ion} , Q_{\oplus} , Q_{Θ} , σ_{\oplus}° and σ_{Θ}° remain constant, and the defect mechanisms are the ones assumed here.

Figure 2.4 shows the relation between electrolytic and ionic domain boundaries in log p_{0_2} , 1/T plane.

A more comprehensive and detailed discussion on the extrapolation of conductivity data may be found in Refs. (10) and (11).


Fig. 2.4 Relation between electrolytic and ionic domain boundaries in the log p₀, 1/T space (from Ref. (11))

2.4. CALCULATION OF THE ACTIVITY OF OXYGEN

FROM THE MEASURED EMF

When solid coexisting metal-metal oxides, such as $Cr-Cr_2O_3$, are used as the reference electrode, the oxygen concentration cell may be represented as follows:

Mo
$$\begin{vmatrix} Cr-Cr_2O_3 \\ VDT \end{vmatrix}$$
 $\begin{bmatrix} CSZ \\ or \\ YDT \end{vmatrix}$ $\begin{bmatrix} M \end{bmatrix}$, $\begin{bmatrix} O \end{bmatrix}$ in liq. Fe $\begin{vmatrix} MO \\ MO \end{vmatrix}$ (IV)

where the reference electrode is written on the left hand side by convention.

The cell reaction for the above cell is

$$[0]_{1wt} + \frac{2}{3} Cr(S) = \frac{1}{3} Cr_2 O_3(S)$$
 (2.40)

for which

$$\Delta G_{(2.40)} = \Delta G^{\circ}_{(2.40)} + RT \ln \frac{1}{h_0}$$

= -2EF . (2.41)

 $\Delta G^{\circ}_{(2.40)}$ is the standard free energy change for the reaction (2.40), and it can be represented as the difference of the free energy changes for the following reactions:

$$\frac{1}{2} O_2(g) + \frac{2}{3} Cr(S) = \frac{1}{3} Cr_2 O_3(S)$$
 (2.42)

$$\frac{1}{2} O_2(g) = [O]_{1wt}$$

Therefore,

$$\Delta G^{\circ}_{(2.40)} = \Delta G^{\circ}_{(2.42)} - \Delta G^{\circ}_{(2.43)}$$

= RT ln $p_{0_2}^{1/2}$ + RT ln K (2.43)
= RT ln K (2.43) $p_{0_2}^{1/2}$ (2.44)

where $K_{(2.43)}$ is the equilibrium constant for the reaction (2.43) and P_{0_2} is the oxygen partial pressure in equilibrium with $Cr-Cr_20_3$ at temperature T.

Solving Eq. (2.41) for $\ln h_0$ in terms of E and substituting Eq. (2.44) for $\Delta G^{\circ}_{(2.40)}$, one obtains

$$\ln h_0 = \frac{2EF}{RT} + \ln K_{(2.43)} p_0^{1/2} . \qquad (2.45)$$

Replacing $\ln h_0$ with 2.3 log h_0 and substituting a value of 1.98 for R, the result will be

$$\log h_0 = \frac{2EF}{4.574 T} + \log K_{(2.43)} p_{0_2}^{1/2} . \qquad (2.46)$$

The explicit form of Eq. (2.46) as a function of E and T can be evaluated using the available data for $K_{(2.43)}$ and p_{O_2} .

(2.43)

Alternatively, $\Delta G^{\circ}_{(2.40)}$ in Eq. (2.41) may be expressed as a function of temperature in the general form of

$$\Delta G^{\circ}_{(2,40)} = A + BT , \qquad (2.47)$$

thus making it possible to rewrite Eq. (2.41) in the following form

$$-A - BT + RT \ln h_0 = 2EF$$
 (2.48)

or

$$\log h_{O} = \frac{2FE + A}{4.574 T} + \frac{B}{4.574}$$
(2.49)

where A and B are constants.

Figure 2.5 shows the graphical representation of Eq. (2.49) using the data given in Ref. (62); i.e.,

$$\log h_0 = 4.52 - \frac{(13,300 - 10.08 E)}{T}$$
(2.50)

where E is in mV and h_0 is the Henrian activity of oxygen, which may be taken equal to weight percent oxygen in the Fe-O system, i.e., $f_0^\circ = 1$ ^(13,17).





OXYGEN, ppm +

2.5. CALCULATION OF THE ACTIVITY OF ALLOYING ELEMENTS FROM THE MEASURED EMF

From the measured EMF of cell IV (p. 24) the activity of any alloying element in the melt can be calculated, provided that the melt is in equilibrium with an oxide phase of that alloying element.

If the oxide is solid at steelmaking temperatures and has the general form of M_2O_x ; where M stands for the alloying element, and x its valency state, the following cell reaction may be considered.

$$\frac{3}{2} \times M_2 O_x(S) + Cr(S) = \frac{3}{x}[M] + \frac{1}{2} Cr_2 O_3(S)$$
(2.51)

where the standard state for the alloying element on the right hand side of Eq. (2.51) is taken to be the pure solid element, and the reference electrode is $Cr(S)-Cr_2O_3(S)$.

The free energy change for the reaction (2.51) is

$$\Delta G_{(2,51)} = \Delta G^{\circ}_{(2,51)} + RT \ln Q_{(2,51)}$$

 $= \Delta G^{\circ}_{(2.51)} + \frac{3}{x} RT \ln a_{M} , \qquad (2.52)$

 $\Delta G^{\circ}_{(2.51)}$ being the standard free energy change, Q the quotient of activities of the products to the reactants in Equation

(2.51), and a_{M} the Raoultian activity of M. Just as before, $\Delta G_{(2.51)}$ and $G_{(2.51)}^{\circ}$ are related to the EMF by:

$$\Delta G_{(2.51)} = -3E_{cell} F$$
 (2.53)

anđ

$$\Delta G^{\circ}_{(2,51)} = -3E^{\circ}F$$
 (2.54)

where E_{cell} and E° are in volts.

Combining Eqs. (2.53) and (2.54) with Eq. (2.52) and changing the log base to 10, one may write

$$\log a_{M} = \frac{xF}{4.575 T} (E^{\circ} - E_{cell}) . \qquad (2.55)$$

2.6. CRITERIA FOR APPLICABILITY

For a galvanic cell with a solid electrolyte to operate successfully and reliably at high temperatures, one may establish the following criteria:

(a) The galvanic cell must be reversible in establishing local equilibrium at the electrode-electrolyte interface ⁽¹²⁾; that is, if the results obtained are to be predicted by relations presented so far.

(b) There should be no concentration gradient in the electrodes, otherwise the EMF readings obtained correspond to an undefined potential ⁽¹²⁾.

(c) There should be no reaction involved other than the one described by the cell reaction. Any reaction between the electrolyte and the electrodes, or between the electrodes and the surrounding atmosphere rules out the use of simple equations such as Eqs. (2.2) and (2.31).

(d) The ionic transport number of the electrolyte should be virtually 1, otherwise short circuiting of the cell will take place, even under open circuit conditions. In this case, the charge carried by oxygen transported forms the exact equivalent of the charge leak-through by the electronic conductivity, and as reported in Ref. (39), it can be expressed in terms of a current by an equation derived by

Wagner for the case of a growing oxide layer on a metal during oxidation. This equation can be written as (39):

$$-j_{e} = j_{ion} = (\sigma_{t} t_{e} t_{ion}/4F) \text{ grad } \mu_{(O_{2})}$$

$$= (1/4F) \cdot [\sigma_{ion}\sigma_{e}/(\sigma_{e}+\sigma_{ion})] \text{ grad } \mu_{(O_{2})}$$

$$(2.56)$$

$$(2.56)$$

$$(2.57)$$

(e) Thermal EMF and contact potentials must be negligible ⁽⁵⁾.

2.7. LOCAL THERMODYNAMIC EQUILIBRIUM AND THE REVERSIBILITY TEST

All the relationships derived between EMF and the associated free energy changes require local thermodynamic equilibrium to be maintained at the relevant phase boundaries ⁽¹²⁾. It is, therefore, necessary to ensure that the galvanic cell is behaving reversibly; this is accomplished by passing a small current through the cell in either direction and noting whether the observed voltage returns to the original value recorded before the cell equilibrium was disturbed.

2.8. POLARIZATION

This phenomena is the major source of error in work involving solid electrolytes. The problem may arise due to the internal "short circuiting" behaviour of the solid electrolyte, which allows oxygen to be transferred within the electrolyte from one electrode to the other in the same direction as the imposed oxygen chemical potential gradient, that is, from the cathode to the anode. Unless the relevant chemical reactions and mass transfer processes are sufficiently rapid, at the point at which the electrode is in contact with the electrolyte, its particles at the surface can become oxidized, and the oxygen potential can thus rise above that for equilibrium with the relevant metal-metal oxide. In this case, if the equilibrium is disturbed, the electrode system may readjust to a different steady state condition corresponding to an undefined higher oxygen chemical potential and the cell EMF will be reduced accordingly (12).

2.9. ACCURACY OF A GALVANIC CELL

If Eq. (2.2) is differentiated,

$$\delta \Delta G = -nF(\delta E) \tag{2.58}$$

so that for a virtual chemical cell reaction a one millivolt uncertainty in the cell voltage corresponds to 23n calories uncertainty in ΔG . This is 46 cal. for n=2 and 92 cal. for n=4.

In the absence of any special problems, careful experimentations can achieve measurements of this accuracy ⁽⁵⁾.

2.10. DEOXIDATION EQUILIBRIA IN Fe-M-O SYSTEM

When deoxidizing elements are used to deoxidize steel, there is usually more than one possible deoxidation product. The condition under which a particular deoxidation product is present depends on the residual deoxidant content and the temperature.

In order to determine the above conditions, one must consider the equilibrium relations pertinent to a given deoxidation process. In most systems of interest, one of the oxides is a spinel of the form $Fe0.M_2O_x$, and the other is an oxide of the general form M_2O_x . Here, M stands for the deoxidant, and x for its valency state. Although the treatment here will only be confined to a case where the two oxides cited above are the only deoxidation products, the procedure is equally applicable to cases with more than two deoxidation products and/or different valency states.

At a given temperature, any one of these oxides is only stable within a certain range of oxygen activity. For deoxidant levels for which the spinel is the stable product, one may write

 $Fe(l) + 2[M]_{lwt} + (x+1)[O]_{lwt} = FeM_2O_{(x+1)}(S)$ (2.59)

for which the equilibrium constant is

$$K_{(2.59)} = \frac{1}{h_M^2 \times h_O^{(x+1)}}$$
 (2.60)

For deoxidant levels for which $M_2^0_x$ is the stable product, one may write

$$2[M]_{1wt} + x[0]_{1wt} = M_2 O_x(S) . \qquad (2.61)$$

The equilibrium constant for Eq. (2.61) is

$$K_{(2.61)} = \frac{1}{h_M^2 \times h_0^x}$$
 (2.62)

Taking the log of both sides of Eq. (2.60) one obtains:

$$\log K_{(2.59)} = -(2 \log h_{M} + (x+1) \log h_{O})$$
 (2.63)

and solving for log h_M:

$$\log h_{M} = -\frac{1}{2} \log K_{(2.59)} + \frac{x+1}{2} \log h_{O}$$
 (2.64)

Similarly for Eq. (2.62)

$$\log h_{M} = -\frac{1}{2} \log K_{(2.61)} + \frac{x}{2} \log h_{O} \quad . \tag{2.65}$$

If log h_{M} is plotted against log h_{O} , straight lines are obtained with slopes of (x+1)/2 and x/2, and intercepts of $-1/2 \log K_{(2.59)}$ and $-1/2 \log K_{(2.61)}$ for melts in equilibrium with the spinel and M_2O_x , respectively.

This means that the deoxidant-oxygen relationship in liquid iron is represented by two or more lines which intersect at that activity of oxygen where the melt is in simultaneous equilibrium with both oxides, i.e., points A, B, C and D shown in Fig. 2.6. This behaviour is shown by vanadium, chromium, aluminum and other elements which form a series of oxides when added as deoxidants.

In general, the spinel oxide has a lower interfacial energy in steel than the M_2O_x . The oxide M_2O_x is thus more readily absorbed by a slag cover than the spinel and is removed from the liquid steel ^(1,2). In the production of clean steel it is essential that the formation of the spinel type oxide should be avoided. Deoxidation should, therefore, occur through the formation of the M_2O_x oxide, at oxygen activities less than those given by points A, B, C and D in Fig. 2.6. A knowledge of these transition points is thus essential to successful deoxidation.

Several methods can be used to determine the position of these transition points. These methods can be classified into (a) Indirect and (b) Direct methods.

(a) The Indirect Method: This method consists of equilibrating an Fe-M-O melt with an oxidizing gas, such as H_2/H_2O or CO/CO_2 gas mixture, at steelmaking temperatures, and suddenly quenching the melt, analyzing for [O], [M] and



LOG h_M +

Fig. 2.6 Schematic representation of the deoxidation diagram for Fe-M-O system. Points A, B, C, D indicate the oxygen activities at the spinel-M₂O_x transition point identifying the oxide in equilibrium with these elements. If the results of such experiments are plotted either as $\log(p_{H_2}/p_{H_2O})$ versus $\log h_M$ or $\log h_O$ versus $\log h_M$, straight lines will be obtained ^(13,57,58), as described in Section 2.10. Interpolation of the straight lines for two different oxides at low and high deoxidant content, will give the transition oxygen activity at the point the two lines meet.

(b) The Direct Method: This method is based on the direct measurements of the transition oxygen potential using solid state galvanic cells.

Since, from a kinetic point of view, it takes time for one oxide to transform into another upon deoxidation or oxidation, then the activity of oxygen can be monitored continuously to detect this transition in situ.

If Eq. (2.59) is subtracted from Eq. (2.61) one obtains

$$FeM_{2}O_{x+1}(S) = M_{2}O_{x}(S) + [O]_{lwt} + Fe(l)$$
 (2.66)

the equilibrium constant for which is

$$K_{(2.66)} = \frac{h_0 \times a_{M_2}O_x}{a_{FeM_2}O_{x+1}}$$
 (2.67)

If $M_2^{O}(S)$ do not form a solid solution with the solid spinel at steelmaking temperatures, Eq. (2.67) reduces to

$$K_{(2.66)} = h_0$$
 (2.68)

Equation (2.68) indicates that the oxygen activity remains constant at the transition point until one oxide is completely transformed into the other. Since, according to Eq. (2.49) (§2.4) E_{cell} is proportional to log h_0 , then measurements of E with time should show a plateau during oxidation or deoxidation at which $\partial E/\partial t = 0$, as shown in Fig. 2.7.

In order to determine how the transition point varies with temperature, one should refer back to Eq. (2.68). Expressing log $K_{(2.66)}$ as a function of temperature, one may write

$$\log h_0^T(T) = \log K_{(2.66)}(T) = \frac{-A}{T} + B$$
 (2.69)

where A and B are constants, and $h_0^T(T)$ and $K_{(2.66)}^{(T)}$ represent the transition oxygen activity and the equilibrium constant as a function of T, respectively.

A plot of log $h_0^T(T)$ versus 1/T is a straight line with a slope -A and an intercept B. These constants can be derived from the free energy change of Eq. (2.66). Figure 2.8 schematically shows a deoxidation diagram in threedimensions.









Fig. 2.8 Three dimensional representation of the deoxidation diagram in Fe-M-O system (NOT TO SCALE)

CHAPTER 3

LITERATURE REVIEW

3.1. EQUILIBRIUM IN Fe-V-O SYSTEM

In 1951 Chipman and Dastur (57) were the first to report an equilibrium study in the Fe-V-O system at 1600°C. They equilibrated Fe-V melts with H_2O/H_2 gas mixtures and gradually increased the H_2O/H_2 ratio until some of the dissolved vanadium was oxidized and appeared as a thin oxide film on top of the melt. They mixed one part of hydrogen to four parts of argon in the gas mixture to prevent thermal diffusion. At the end of the run, the ingot was quenched, by lowering it into a cooler region of the furnace. The oxide products were identified by X-ray diffraction, as FeV_2O_4 and V_2O_3 . The former, which is the spinel, was found in two ingots of 0.1% V, and the latter was found on ingots containing more than 0.35% V.

Based on their identification of the oxide products, the corresponding reactions were written as

$$FeV_{2}O_{4}(S) + 4H_{2}(g) = 2[V] + Fe(l) + 4H_{2}O(g)$$
 (3.1)

$$K_{(3.1)} = h_V^2 \left(\frac{p_{H_2O}}{p_{H_2}}\right)^4$$
 (3.2)

and

$$V_2O_3(S) + 4H_2(g) = 2[V] + 4H_2O(g)$$
 (3.3)

$$K_{(3.3)} = h_V^2 \left(\frac{p_H_2 0}{p_H_2}\right)^3$$
 (3.4)

for low and high V-concentration, respectively. A plot of $\log(p_{H_2O}/p_{H_2})$ versus $\log h_V$ yielded straight lines with slopes of 1/2 and 2/3 corresponding to the FeV₂O₄ and V₂O₃ equilibrium product, respectively, although there was some deviation from linearity at high vanadium levels. They attributed this to a departure from Henpry's law, or to a possible third lower oxide phase. Since they could not find any evidence of this oxide in their investigation, they finally regarded the deviation as the result of experimental inaccuracy.

By interpolating the two lines drawn through their data, they found that the composition at which the two oxide phases coexist in equilibrium with the melt at 1600°C was 0.17% V.

It is reported (13,58) that Karasev et al. studied the same system at 1595 and 1695°C with a similar technique. Using X-ray diffraction, they identified FeV₂O₄ as the oxide phase for vanadium contents up to 0.2% and V₂O₃ at higher vanadium concentrations. Having plotted log(p_{H2}O/p_{H2}) versus log h_V, they observed that the slope of the line was very close to unity at high concentrations of vanadium

(>0.3%), and so they concluded that above 0.3\% V the stable oxide was the vanadium monoxide, VO or V_2O_2 . Although V_2O_2 was not identified by X-ray diffraction, they argued that it decomposed during quenching and the resulting vanadium was oxidized to V_2O_3 . This observation seems to be in line with the work of Chipman and Dastur.

Narita and Kayama ⁽⁵⁸⁾ studied the same deoxidation equilibrium, at 1600, 1650 and 1700°C, using X-ray and electron diffraction techniques. The latter technique was used at the equilibrium temperature, as well as on the oxides extracted from ingot samples. They identified FeV_2O_4 and V_2O_3 as the deoxidation products for low and high vanadium contents respectively.

In 1970 Fruehan ⁽²¹⁾ reported the same deoxidation products at 1600°C, using the following solid electrolyte galvanic cells

Mo $Cr-Cr_2O_3$ CSZ Fe-V-O (ℓ , sat'd with oxide) Mo (V) and Mo $Cr-Cr_2O_3$ YDT Fe-V-O (ℓ , sat'd with oxide) Mo (VI)

In plotting his data as $log(w/0 \ 0)$ versus $log(w/0 \ V)$, he found at about 0.1 w/0 V the experimental line approached a slope of -1/2, indicating FeV_2O_4 . Mixed $FeV_2O_4-V_2O_3$ oxides were assumed to be the deoxidation product in the range 0.1 - 0.39 w/0 V, and above 0.3 w/0 V he found only V_2O_3 .

Kay and Kontopolous ⁽⁵⁹⁾ using a similar method to that of Fruehan, plotted their H_2O/H_2 equilibration ⁽¹³⁾ and galvanic cell data as log h_O versus log h_V . Two lines with slopes of -1/2 and -2/3 fitted their data for low and high vanadium content, respectively. By interpolation, they set the FeV₂O₄-V₂O₃ transition point at 0.2, 0.30, 0.47 and 0.75 w/0 V at 1550, 1600, 1650 and 1700°C respectively. They did not identify V_2O_2 in this work.

It may be worth while indicating that a series of similar studies ^(21,22,58) on the equilibrium deoxidation products using Nb, Ta, B, Al, Ti and Cr indicate the existence of transition points during deoxidation.

After studying the removal of deoxidation products from steel, McLean and Ward ⁽²⁾ concluded that only the M_2O_x type of oxides can readily separate in liquid steel due to a higher interfacial tension compared to that of FeO.V₂O₃. Thus, they emphasized that due consideration must be given to this phenomenon during steel deoxidation.

3.2. SOLID ELECTROLYTES

3.2.1. Introduction

Though solid electrolytes were being used as early as 1900 (12), the work of Kiukkola and Wagner (3,4) and Lidiard (14) stimulated a general revival of interest in high-temperature galvanic cells incorporating these electrolytes.

Prior to 1957, most of the solid electrolytes were for relatively low temperature applications, whereas after 1957 more attention was given to refractory electrolytes, especially oxide electrolytes, for their potential use in steelmaking in the determination of high temperature thermodynamic data.

Table 3.1 presents a list of low temperature solid electrolytes taken from Ref. (14).

Because of the immediate relevance of the refractory oxide solid electrolytes to deoxidation, only these will be dealt with here.

47[·]

TABLE 3.1

ILLUSTRATIVE VALUES OF TRANSPORT NUMBERS IN A VARIETY

OF COMPOUNDS

Solid	Electrolyte	Temperature	t ₊	ˈt_	t
	1	(°C)	·		
	NaF	550	1.00	0.00	
	NaCl ·	400	1.00	0.00	
	NaBr	435	0.96	0.04	
	KCl	435	0.96	0.04	-
KCl +	0.2% CaCl ₂	430-600	0.99	0.01	-
	KBr	605	0.50	0.50	
	KI	610	0.90	0.01	•••
	AgCl	20-350	1.00	-	
	AgBr	20-300	1.00		-
	a-AgI	150-400	1.00	-	-
	β -AgI	20 -140	1.00		-
	BaF.2	500		1.00	42
	BaC12	400 -700	1.199	1.00	هنب
	BaBr ₂	350 -450	-	1.00	ي تحد
	PbF ₂	200		1.00	
	PbC12	200 -450	-	1.00	635
	PbBr ₂	250-365		1.00	
	PbI2	255	0.39	0.61	
	CuCl	18	0.00	canas	1.00
	r-CuBr	27	0.00	-	1.00
1	3-CuBr	395-445	1.00		-
	γ-CuI	200	0.00		1.00

3.2.2. Solid Oxide Electrolytes

Kiukkola and Wagner ⁽⁴⁾ presumed that the concentration of excess electrons and electron holes in solid oxide electrolytes are determined by the oxygen partial pressure of the surrounding atmosphere by virtue of the reactions (2.16) and (2.17) (p. 14). In view of the low total conductivity, they assumed that the concentration of anion vacancies and valence electrons are virtually independent of the external oxygen pressure. Hence, on applying the ideal law of mass action to Eqs. (2.16) and (2.17) they wrote

$$C_{\theta} = C_1 p_{0_2}^{-1/4}$$

and

$$C_{\oplus} = C_2 p_{O_2}^{1/4}$$
 (3.6)

where C_{Θ} and C_{Θ} are the concentration of excess electrons and electron holes respectively, and C_1 and C_2 are constants.

They pioneered extensive research in this field, using AC conductivity measurements to characterize solid (oxide) electrolytes. After establishing that $0.85 \text{ } \text{ZrO}_2 + 0.15 \text{ CaO}$ had a constant conductivity for a given range of oxygen partial pressures, they checked the validity

(3.5)

of their results by determining the free energy of formation of a number of oxides and comparing them with the results from gas equilibrium studies ⁽⁴⁾.

Since 1957, this procedure has become the standard method of checking the performance of electrolytes, and determining their domain of ionic conduction.

Today, solid electrolytes are extensively used in different forms in industry ^(19,35,36) and research ^(18,20,26), details of which will be given in later chapters.

3.2.3. Electrolytes and Electrodes Used in this Work 3.2.3.1. <u>0.85 $ZrO_2 + 0.15$ CaO Electrolyte</u>: This is the most commonly used electrolyte and has been extensively used for relatively low temperature (around 1000°C) studies. During the recent years more and more results are appearing in the literature regarding the use of this electrolyte at steelmaking temperatures (1600°C).

The oxygen partial pressure range within which a $t_{ion} > 0.99$ prevails at 1000°C is set between 1 and 10^{-17} atm. by Steele and Alcock ⁽⁹⁾, though in a later study, a higher upper limit of 100 atm. is reported ⁽¹⁵⁾. The lower limit is in very close agreement with the estimated values of Baker and West ⁽¹⁶⁾.

A great controversy develops when one considers the boundaries of ionic domain at steelmaking temperatures. Although Baker and West (16) suggested little use for CSZ at steelmaking temperatures, Schwerdtfeger (18), Fitterer (19) and later Fruehan et al. (17) have reported successful results.

The most recent treatment of all the works done on CSZ is that of Patterson (10). After theoretically finding the domain of ionic conductivity, as described in Section 2.3.1, he compiled the existing data up until 1971, and plotted them in log P_{0_2} , 1/T planes, in order to find the ionic boundary, as shown in Fig. 3.1. He used the results of Baker and West (16) and Schmalzried (65) to calculate the position of his theoretical line, and in this way the results of Tretyakov (66), Fischer and Janke (67), Borgren and Rapp (8), Patterson and Rapp (8), Smith et al. (68)and Fruehan et al. (17) are all shown to be out of the 99 percent ionic domain, both at low and high temperatures.

Despite the discrepancies in results of some of the investigators, cited above, satisfactory performances of CSZ electrolytes in liquid steel have been achieved by Sanbongi et al. $^{(24)}$ in Fe-C-O melts at 1600°C, by Matsushita et al. $^{(25)}$ in medium carbon and carbon saturated melts at 1550°C, by Fruehan et al. $^{(17)}$ and Fruehan $^{(20-23)}$ in a series of deoxidation equilibrium measurements, and finally by Kontopolous $^{(13)}$ who used this electrolyte to study the deoxidation equilibrium in the Fe-V-O system, at 1550, 1600, 1650 and 1700°C.





* Present work

The results of these investigators indicated that CSZ was virtually an ionic conductor even down to an oxygen partial pressure of 3 \times 10⁻¹³ atm. at 1600°C.

The conductivity measurements of Kingery and coworkers $^{(38)}$, Johnson and Cleary $^{(37)}$ and recently Heyne and Beekmans $^{(39)}$ revealed a p₀ dependence of the electronic conductivity, as predicted by Kiukkola and Wagner $^{(4)}$. The temperature dependence of the conductivity is established to be of the Arrhenius type $^{(37,38)}$. Heyne and Beekmans $^{(39)}$ developed a conductivity diagram for CSZ which is shown in Fig. 3.2.

3.2.3.2. $\underline{\text{ThO}}_2$ (YO_{1.5}) (90:10 mole ratio) Electrolytes: Because of the lower oxygen partial pressure boundary for ionic conduction, YDT has found application in studies of highly deoxidized steel. Fruehan and coworkers ⁽¹⁷⁾, and Fruehan ^(17,22,23) have used this electrolyte for all their measurements in Fe-Cr-O, Fe-Ti-O, Fe-V-O, Fe-B-O and Fe-Al-O systems for oxygen partial pressures below 3 × 10⁻¹³ atm. Using a ThO₂(7 w/O Y₂O₃) in Fe-Si melts, they found out that the electrolyte exhibited insignificant electronic conductivity at oxygen partial pressures as low as the Si-SiO₂ equilibrium, i.e., 9.5 × 10⁻¹⁸ and 2 × 10⁻¹⁶ atm. for 1550 and 1600°C, respectively ⁽²³⁾.







Unfortunately there is little information available in the current literature about the use of YDT solid electrolytes at steelmaking temperatures. Lidster and Bell ⁽²⁶⁾ determined the thermodynamic properties of Cralloys using ThO₂(4-5% Y₂O₃), for 1020 - 1430°C. Their conductivity measurements indicated ionic behaviour for this electrolyte at oxygen partial pressures of 10^{-6} to 10^{-20} atm. at 1100°C and down to 10^{-25} atm. at 800°C. It is interesting to note that their results indicated mixed conduction for air as electrode, at all temperatures (800 - 1100°C) investigated. This may partially explain why Subbaro et al. ⁽⁴⁴⁾ encountered mixed conduction in their attempt to establish the ionic range of YDT with air reference electrodes. The results of Lidster and Bell agree quite well with the later work of Tretyakov and Muan ⁽¹⁵⁾.

Patterson in a similar method to that cited before for CSZ, compiled all the data for the ionic-electronic boundary of YDT, obtained prior to 1971, in order to establish the ionic domain boundaries for this electrolyte. Although his treatment showed very good agreement among different authors for temperatures between 700°C and 1100°C, his estimated ionic conduction boundary at 1600°C lies outside the range of the oxygen partial pressures encountered in steelmaking.

Needless to say, the results of Schwerdtfeger (18)and Fruehan (17,22,23) on YDT do not fall inside this

boundary, which is obtained by extrapolation of low temperature data, as shown in Fig. 3.3. However, EMF measurements by Schwerdtfeger, and by Fruehan, and other investigators, involving YDT and liquid iron alloys, indicate that a very significant range of oxygen partial pressures encountered in steelmaking lies within the electrolytic domain of YDT. The discrepancy may be because of the difference in dopant concentration or the level of impurities in the electrolytes used.

Obviously, this disagreement regarding the location of the low p₀ electrolytic domain boundary, especially in the neighbourhood of 1500 - 1600°C, indicates that it is not wise to extrapolate low temperature results, with the lack of a consistent conductivity and/or EMF data. This is why Patterson's treatment gave too conservative a result compared to what is actually found in practice.

The conductivity behaviour of YDT is similar to (40), i.e., its electronic conductivity shows the same pressure dependence, and its variation with temperature is Arrhenius type. Figure 3.4 shows, schematically, how the conductivity of YDT is affected by the dopant concentration.

3.2.3.3. <u>Reference Electrodes</u>: Early investigators ^(16,27,28) have predominantly used air or gas mixtures as reference electrodes for CSZ. An air reference cannot be used for







Fig. 3.4 Schematic illustration of the effect of dopant concentration on partial conductivities in ThO₂-MO_{1.5} solid solutions
YDT ⁽²⁶⁾ because of electron hole conductivity at such high oxygen partial pressure. Furthermore, even in the case of CSZ using air as the reference electrode gives rise to high EMF readings; as a result the determination of oxygen in steel becomes less accurate ⁽¹⁷⁾. For a higher accuracy the oxygen partial pressure of the reference electrode should be in a range comparable to that of oxygen in steel.

Reference electrodes that have found applications may be classified as follows:

(a) Direct (Reference) Electrodes: are those that establish oxygen partial pressure as a function of composition only, such as O₂, Ag, etc., or any mixture of oxygen with an inert gas.

Air was employed by Fitterer ⁽²⁸⁾, Schwerdtfeger ⁽¹⁸⁾, Baker and West ⁽¹⁶⁾ and Ag was used by Kiukkola and Wagner ⁽⁴⁾.

(b) Coexisting Electrodes: which involves two condensed or gaseous phases in coexistence, such as Fe-FeO, Cr-Cr₂O₃, Ni-NiO, and gas mixtures such as CO-CO₂, H₂-H₂O.

A cell using this type of electrode that is of particular interest may be written as

Mo
$$|Cr(S)-Cr_2O_3(S)|$$
 YDT or CSZ $|Fe-M-O|$ Mo (VII) (liquid)

where M stands for an alloying element.

The condensed phase coexisting electrodes have been used by several authors (4,9,13,23,28) for determination of thermodynamic data.

(c) Indirect (Exchange) Electrodes: This type of electrode is used in cells in the determination of reaction thermodynamics, involving an ion for which a solid electrolyte is not available ⁽⁵⁾. In the following cell, Ag₂S is an example of an indirect (exchange) electrode:

The electrode Ag_2^S is an electronically conducting compound with a very high silver diffusivity and well known $\Delta G^{\circ}_{Ag_2^S}$. If the electrodes containing sulfur are equilibriated, the voltage of cell VIII, which directly compares Ag activities in the electrodes, can then be related to the sulfur activity in the right hand electrode according to the relation

$$E = -RT \ln a_{Ag}(Ag_2S) = \frac{RT}{2} \ln a_S(Ag_2S) - \frac{1}{2} AG_{Ag_2S}^{\circ}$$
 (3.7)

The indirect (exchange) electrode then serves as a phase in which the activity of the component of interest can be related to the activity of another component for which a solid electrolyte exists.

3.2.3.4. <u>Cell Design</u>, Procedures and Precautions for <u>Equilibrium Measurements</u>: The most acceptable experimental cell geometry for a given measurement is one which best eliminates the occurance of mixed (multiple) half cell reactions $^{(5)}$. It is well understood that the electrode and electrolyte should neither partake in any reaction other than the cell reaction, nor should they interdiffuse significantly to provide mutual contamination $^{(4)}$.

Except when further experimental checks are impossible, no cell voltage should be assumed correct just because a steady value is obtained experimentally ⁽⁵⁾.

A method of checking that a steady cell voltage is the equilibrium value is to obtain the same value, whether a temperature is reached by heating or cooling (5,14). The reversibility of the apparently stable voltage should be tested by passing a small current through the cell in either direction, and noting if the voltage will approach that EMF before disturbing (5,31). The cell voltage should not be influenced by the rate of gas flow over the cell; otherwise interaction or cooling effects are indicated (5). In the following sections, some points concerning experimental techniques with specific relevance to cells with solid, liquid and gaseous electrodes are discussed.

3.2.3.4.1. Cells with Solid Electrodes: If a galvanic cell involves solid electrodes for which no gas phase interaction is expected, then the electrodes and the electrolyte may be formed or fabricated into small cylinders or disks which are pressed together in a cell holder. A cell of this type is

shown in Fig. 3.5 which was originally constructed by Kiukkola and Wagner ⁽⁴⁾ and it has been employed by several other authors, with some modifications ^(26,28,56), for determination of thermodynamic data and conductivities at relatively low temperature (<1000°C). If the electrodes are sensitive to gas-phase interactions, one or both electrodes must be isolated from the surrounding gas atmosphere ⁽⁵⁾. Electrode isolation has been cheaply and easily accomplished by Schmaltzeried ⁽⁵⁾ and Rapp ⁽¹³⁾. These investigators have used CSZ electrolyte bodies which contained deep holes into which the powdered electrode material is pressed and capped. Figure 3.6 depicts various designs that were used to isolate the electrodes from the surrounding atmosphere.

3.2.3.4.2. Cells with Liquid Electrodes: It has been shown by several investigators that CSZ and YDT electrolytes perform satisfactorily for liquid metals such as copper ⁽³¹⁾, silver ^(30,31), lead ⁽²⁹⁾ and moderately deoxidized iron melts ^(17,24). YDT can even be used for highly deoxidized steels with oxygen partial pressures as low as that in equilibrium with Si(ℓ)-SiO₂(S) at 1600°C (2 × 10⁻¹⁶ atm.) ⁽¹⁷⁾.

Early applications of these cells to determine thermodynamic data for liquid metals were electrolytes in the form of tubes ^(18,24,31) and sometimes crucibles ⁽³³⁾. But because of poor thermal shock resistance and the high cost of these tubes, they could not be used commercially to



Fig. 3.5 Cell design for EMF measurements.



(a)



Fig. 3.6 Cells with separate electrode compartments (from Ref. (12))

monitor oxygen activity in liquid steel. This problem was resolved by Fitterer (28), who developed a probe consisting of a silica tube sealed at one end with a small cylinder of $2rO_2$ (CaO) electrolyte with gas reference electrode. Such probes had good resistance to thermal shock and are relatively inexpensive to manufacture (19). A similar type of probe using air as the reference electrode was developed and tested on a laboratory and industrial scale by the Mines Branch of the Department of Energy, Mines and Resources of Canada (34). This became commerically available through Leigh Instruments Ltd. of Carlton Place, Ontario.

However, the use of air or CO_2 as the reference electrode has a number of disadvantages ⁽¹⁷⁾. These disadvantages have been resolved by Fruehan and coworkers ⁽¹⁷⁾, who found that a mixture of $Cr(S)-Cr_2O_3(S)$ appeared to be a suitable choice of electrodes compatible with CSZ and YDT electrolytes. Using this mixture as the reference electrode, they developed the U.S.S. probes, which has apparently performed satisfactorily in industry ^(35,36), using a similar technique to that employed for the immersion thermocouple.

Figure 3.7 shows the various cell designs employed in research laboratories and Fig. 3.8 shows the design of the immersion probes used to measure temperature and oxygen activity, simultaneously.

EMF measurements in liquids involve some experimental problems. The electrode lead wire which contacts the melt







Fig. 3.8 Photograph of the U.S.S. oxyprobes designed to measure the temperature and oxygen activity, simultaneously, at steelmaking temperatures must be chosen carefully to avoid undesirable side reactions. The material for this purpose should be insoluble in the melt or else dissolve quite slowly; by dissolving, it should not add or remove oxygen from the melt, nor should it affect appreciably the activity coefficient of oxygen ⁽⁵⁾. If the liquid electrode lead wire is a different material from that for the reference electrode, then the observed voltage must be corrected for the thermoelectric voltage.

3.2.3.4.3. Cells with Gas Electrodes: Another application of solid electrolytes, in particular CSZ, has been to determine the oxygen content of different gas mixtures. A detailed study of gas electrodes has been made by Etsell and Flengas ⁽³²⁾, who studied the performance of CSZ electrolytes with different gas mixtures under several conditions of temperature and pressure.

CHAPTER 4

MANUFACTURE OF YDT CRUCIBLES

4.1. MATERIALS AND SOLID SOLUTION PREPARATION

A literature review of the preparation of dense $ThO_2-Y_2O_3$ reveals that the initial particle size plays an important role in determining the final density and sinterability ^(41,42). In a thorough literature search up to 1970, Anderson ⁽⁴²⁾ pointed out that the preparation of thoria and yttria for ceramic manufacture has been directed towards the preparation of small diameter particles of "active" powders.

In a sintering study of ThO_2 obtained from hydroxide, carbonate, nitrate and oxalate solutions, Kantan et al. ⁽⁴¹⁾ reported that the thoria obtained from thorium-oxalate solutions yielded a fine precipitate and a maximum density. These results were later confirmed by Subbaro et al. ⁽⁴⁴⁾, Zador ⁽⁴³⁾ and Kontopolous ⁽¹³⁾.

In this work it was decided to coprecipitate thoria and yttria, following the procedure outlined by Zador $^{(43)}$.

The starting materials were thorium nitrate $(Th(NO_3)_4.4H_2O)$ and yttrium nitrate $(Y(NO_3)_3.5H_2O)$ obtained from Fisher Scientific Co. and Alfa Inorganics. The major impurities in the thorium nitrate are shown in Table 4.1 and the yttrium nitrate was of 99.9% purity. A thoria-yttria

TABLE 4.1

MAJOR IMPURITIES IN THORIUM NITRATE USED

Impurity	ppm
Insoluble matter	100
Heavy metals (Pb)	10
Iron (Fe)	10
Titanium (Ti)	100

solid solution of 9:1 ThO₂:YO_{1.5} molar ratio was prepared by coprecipitation.

An aqueous solution of thorium and yttrium nitrate was prepared to contain 11% of their oxides, and the P^H of this solution was adjusted to 1.7 by the addition of dilute NH,OH. A 5 w/0 ammonium oxalate solution in water was also prepared and the P^H adjusted to 3.0 with dilute HNO₃. Coprecipitation was carried out by the addition of a 4 part oxalate to 1 part nitrate solution. The nitrate solution was added to the oxalate at room temperature with vigourous stirring. A milky white precipitate appeared and after adjusting the P^H of this solution to 2.0, the precipitate was left overnight to settle. After decanting the clear portion, the thick precipitate was filtered on Whatman No. 42 filter paper by means of water suction, and then ovendried at 120°C. The precipitate was then ignited at 900°C for about 6 hours. The oxide was ground in a porcelain mortar giving a fine, relatively voluminous, pale brown powder which was reduced to approximately 30% of its volume by subsequent heating to 1200°C in air for 4 hours.

A sample of this powder was mixed with household cement and rolled into a 0.5 mm diameter rod and analysed by X-ray diffraction, using a Debye-Scherer powder technique. The X-ray diffraction pattern of this powder is shown in Table 4.2. A $Cu(K_{\alpha})$ radiation with a Nickel filter was used with 3 hours exposure time for this purpose.

TABLE 4.2

DIFFRACTION PATTERN OF YDT POWDERS

Line No.	Pattern*	^d observed
, 1	VS	3.1870
2	S	2.7719
3	VS	1.9611
4	VS	1.6782
5	MW	1.6029
6	ŅW	1.3896
. 7	S	1.2782
8	S	1.2454
9	S	1.1380
10	S	1.0727
11.	MW	0.9859
12	VS	0.9435
13	S	0.9300
14	S	0.9040
15	MW	0.8521
16	MW	0.8427
17	W	0.8071
18	VS	0.7830

- VS = very strong, S = strong,

MW = medium weak and W = weak.

No diffraction line characteristic of pure yttria was observed indicating a solid solution. Metallographic examination of manufactured crucibles confirmed this finding.

The analysis of the X-ray diffraction pattern gave a value of a = 5.57 Å for the lattice parameter. This is identical to that found by Kontopolous (13), using the similar material, and in good agreement with the work of Hund and Mezgar (45) as reported in Ref. (13).

4.2. SIZE DISTRIBUTION

4.2.1. Theoretical Consideration and Experimental Procedures

In manufacturing dense ceramics, particle size distribution plays an important role in the attainment of maximum density.

A system composed of single-sized particles will pack together to give an average void space of 38%. The introduction of particles of another size, very much smaller than the first, will result in the void space being filled. These smaller spheres will also pack in such a way that 38% of the space occupied by them will in turn be void. The introduction of yet another size, very much smaller than the second, will result in a further decrease in voidage (47).

Based on this principle, Hugill and Rees, as reported in Ref. (47), gave the size distribution for optimum packing and minimum porosity as shown in Table 4.3.

In another work, Murray et al. ⁽⁴⁸⁾ followed the Andreason analysis to obtain dense thoria crucibles and tubes. Andreason found that, if the weight percent undersize (P) and the particle size (x) followed the relation:

$$P = (x/D)^m$$

where D is the maximum particle diameter and m is a constant

(4.1)

TABLE 4.3

THE PROPOSED SIZE DISTRIBUTION OF HUGILL AND REES

Particle Size	w/0 ,
coarse	45
medium	10
fine	45

TABLE 4.4

SIZE DISTRIBUTION FOR MIXTURE A

Size	Mesh w/O	
coarse	-100 + 200	45
medium	-200 + 325	10
fine	-325	45

with a value between 1/2 and 1/3, then a maximum density is obtained.

Figure 4.1 shows the results of Murray et al. ⁽⁴⁸⁾, who obtained crucibles with 97% theoretical density.

Thus, in the light of this information, each of the two grading methods were tried.

4.2.2. Mixture A

This mixture was made up of coarse, medium and fine particles as described in Table 4.4.

The grading was carried out by grinding in a porcelain mortar and sieving. This was repeated until the desired size distribution was obtained.

4.2.3. Mixture B

To obtain a size distribution compatible with Andreason's relationship, Murray et al. ⁽⁴⁸⁾ milled precalcined thoria with steel balls with 4:1 material to ball ratio for 50 hours. In the present work, YDT powder obtained after ignition to 1200°C, was ground in a porcelain mortar. When all the material was sieved through a 200 mesh screen, the size distribution was then adjusted to fit the Andreason relationship, as defined by Eq. (4.1). This was accomplished



by a series of regrinding and sieving until a size distribution close to the theoretical curve was achieved. Size distribution was determined by the Andreason-Lundberg method, details of which are described in Appendix B.

This method is based on the Stokes' law which describes the velocity of a spherical particle falling through a fluid medium, i.e.,

$$v = \frac{1}{18} \frac{(\rho_s - \rho_L) d^2 g}{\eta}$$
 (4.2)

where

v = velocity of the falling particle (cm sec⁻¹) $\rho_{\rm S}$ = density of the solid (g cm⁻³) $\rho_{\rm L}$ = density of the liquid d = particle diameter g = acceleration of gravity (= 981 cm sec⁻²) η = viscosity of the liquid medium (g cm⁻¹ sec⁻¹).

Substituting (H/t) for v and solving for d, one obtains:

$$d = \left[\frac{18\eta}{(\rho_{\rm S} - \rho_{\rm L})g}\right]^{1/2} (H/t)^{1/2}$$
(4.3)

where H is the height of fall (E-F) in cm, and t is the time in sec.

For a
$$\eta$$
 (25°C) = 0.00893 (g-cm⁻¹-sec⁻¹)
 $\rho_{\rm S}$ = 9.16 (g-cm⁻³)
 $\rho_{\rm L}$ = 1 (g-cm⁻³)

one obtains

$$d = 4.31 \times 10^{-3} (H/t)^{1/2}$$
 (4.4)

Substitution of H = 20 cm and expressing t in minutes, gives:

$$d = 2.5 \times 10^{-3} t^{-1/2} [cm] . \qquad (4.5)$$

As shown in Appendix B, each value of d had to be corrected with an appropriate correction factor of $B = [H-x(n-1)]^{1/2}/H^{1/2}$, where H is the initial depth of sampling (20.0 cm), x is the drop in level of the suspension per sample (= 0.42 cm), and n is the number of the samples drawn.

Table 4.5 shows the size distribution analysis obtained by this method, and in Figs. 4.2 and 4.3 the result is plotted as percent undersize versus the corrected particle size.

TABLE 4.5

PARTICLE SIZE DISTRIBUTION OF MIXTURE B

đ *(μ)	d*/D	<pre>% Undersize</pre>
24.5	0.382	76.0
18.4	0.288	71.0
10.8	0.170	61.9
6.7	0.105	45.5
6.0	0.094	29.2
4.3	0.067	14.4
3.3	0.052	1.70
2.4	0.040	1.00
1.8	0.030	0.54
0.6	0.009	0.00

* d* is the corrected particle diameter.



4.3 THE SLIP

A casting slip is a suspension of ceramic materials in water, which can be poured into a dry plaster mold that draws enough water from the slip to increase its strength above that needed to support the cast against the forces of gravity. It is necessary to deflocculate the slip to reduce the water content and to give firmer casts. When sufficient wall thickness is developed, the mold is inverted and the excess slip is poured out.

A good slip should have sufficiently low viscosity to flow readily into the mold, a sufficiently high specific gravity to prevent the settling of larger particles, low drying shrinkage, high green strength after casting and finally freedom from entrapped air. The wall thickness should also increase rapidly.

At the time of writing, no work has been reported in the literature on the slip casting of YDT. The only information available concerne the slip casting of thoria for high temperature use. In 1935 Richardson ⁽⁴⁹⁾ described the manufacture of small cast thoria crucibles using a number of impurities such as cryolite, P_2O_5 and Zirconia to prevent the settling of thoria particles, the clogging of the plaster mold, and to improve the properties of the crucibles, respectively. In 1955, as reported by Hepworth and

Rutherford (50), St. Pierre produced thoria crucibles using polyvinyl as deflocculant and octyl alcohol as an anti-foam agent to decrease the foaming tendency developed on the addition of polyvinyl. Finally in 1965 Murray et al. (48)described preparation of dense thoria crucibles by slip casting. He found that a P^H of 1 gave the best casting properties and no other additive was necessary. It should be mentioned that the maximum particle diameter in this case was 12 μ .

On account of the lack of information on the slip casting of YDT solid solution, systematic measurements were made to determine the correct P^{H} and physical properties of the slip to produce the desired mechanical, chemical and electrolytic properties in the finished crucibles.

Since the addition of any foreign compounds, such as those added by Richardson, was detrimental to the desired ionic properties of the solid electrolyte; HCl and NH_4OH were the only reagents used to adjust the P^H of the solution. In this case, HCl also acted as a deflocculant. Two different slips were made with different characteristics.

4.3.1. Slip A

This slip was made from the mixture A. As stated earlier, the size distribution in this slip was

- 50 + 100 -100 + 200 -200 + 325 -325 meshes

Due to the relatively large particle size, it was difficult to obtain a completely stable slip with no density gradient in the suspension. To find the optimum conditions, slip A was adjusted to a P^H of 8.5 - 9.0 with NH₄OH. This was then slowly reduced by the addition of dilute HCl and the rate of settling noted. At a $P^H \simeq 4.5$ the rate of settling sharply decreased and this proved to be the optimum value. No attempt was made to measure the viscosity of the slip, which was made sufficiently thin for pouring into the mold cavity.

4.3.2. Slip B

This slip was made with a size distribution described by Figs. 4.2 and 4.3. A series of P^{H} measurements indicated that a P^{H} of 1.0 - 1.5 would give the right acidity for a satisfactory slip. In this range of P^{H} the slip was quite stable and did not become thixotropic with time. However, practically all casts made with this slip were defective and the rate of wall thickness development was extremely low (2mm in 10-15 min). All the casts tended to warp on the inside during initial drying, and the outside surface in some cases was covered with blow holes. It is thought that the high acidity of the slip "killed" the plaster mold; gas evolution inhibiting water absorption. In addition, there was virtually no shrinkage in the initial stages of wall development because of the high slip density.

On the other hand, a few crucibles which were not defective cracked during final firing at 1800°C, in an airoxygen-gas furnace. A section at the bottom of one of the crucibles indicated that surface macro-cracks had propagated to a substantial depth below the surface.

Casts made at a basic P^{H} of about 7.5 - 8.0 gave very poor green strength. Most of the crucibles made with this basic P^{H} , cracked, either during drying in air at room temperature, or oven-drying at 30 - 150°C. This was, probably, due to the low specific gravity of the suspension.

At this point the problem was two-fold. A slip had to be made with such a P^{H} as to give a homogeneous suspension, a high enough green strength to handle, and sound physical and mechanical properties after firing. To resolve these problems, crucibles were cast at P^{H_1} s of 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 5.5, 6.0, 6.5, 7.0, 8.0 and 8.5. After initial drying and handling, one or two crucibles were taken from each sound batch, prefired at 1100°C and fired at 1800°C in an oxygen-gas furnace for 3 hours. The results of these trials are shown in Table 4.6, only crucibles made at P^{H} of 5.5 - 6.0 being free from any cracks or boils.

TABLE 4.6

PROPERTIES OF THE MANUFACTURED CRUCIBLES

P^H Range→ 5 → 6 $1 \rightarrow 2.5$ $2.5 \rightarrow 5$ $6 \rightarrow 9$ strength good, strength good, excellent Green very poor warped, no warpage strength, Property some cracks no defects strength good, cracks excellent, Dry some cracks, during no cracks Property 5% shrinkage drying Fired excellent, poor, poor, surface cracks some lateral no cracks Property cracks of any kind Settling very slow fair fast Rate in sluggish Slip

Thus all the subsequent casts were made with a slip of $P^{H} = 5.5 - 6.0$. Out of fifteen crucibles cast at this P^{H} , only two cracked during the final firing in the airoxygen-gas furnace.

Figure 4.4 shows a qualitative diagram for the settling characteristic of YDT slips with a change in P^{H} .



Fig. 4.4 Schematic diagram showing the settling characteristic of YDT particles as a function of P^H (NOT TO SCALE)

4.4. THE MOLD

The mold was made by mixing a 2:1 by weight mixture of plaster to water. A 1:1 mixture suggested by Richardson ⁽⁴⁹⁾ gave a porous mold which had a low water absorption capacity. In contrast a 2:1 mixture gave a denser mold with excellent water absorption. The plaster mold had to be stripped off the master cardboard mold at the start of evolution of the heat of crystallization, otherwise the mold will get pinched and will eventually crack.

The mold could be used many times for slips with P^{H} 's in the range of 4.0 - 6.0, but only once in highly acidic slips.

The crucible patterns were made out of perspex polymer and were coated with paraffin wax to facilitate release from the mold.

4.5. CASTING

Casting was done using the standard slip casting procedure. After vacuum treatment, the slip was carefully and slowly poured into the mold cavity against the side wall. This practice was necessary to obtain a smooth, lamellar flow to prevent air entrapment.

In the case of mixture A a reasonable wall thickness developed after about 4 minutes, after which the mold was inverted and the slip poured out. A few minutes later when the crucible surface was slightly dry, it separated from the mold and could be removed by hand for subsequent drying.

In the case of the casts made from the slip of $P^{H} = 5.5 - 6.0$, excellent water absorption, along with a very good green strength, was achieved. The mold normally had to be inverted in less than 3 minutes to give a wall thickness of about 2-3 mm. Vacuum treatment of the slip was carried out using a rotary vacuum pump, prior to pouring.

After a few moments the cast was freed from the mold, but was held in situ for 3-4 hours.

4.6. DRYING

The formed or green crucibles were dried for one day at each of the following temperatures: 30, 50, 70, 90, 120 and 150°C. This was necessary to prevent cracking.

4.7. PRELIMINARY SINTERING

After drying, the crucibles were removed from the oven and placed in an air muffle furnace at 150° C. The temperature of the furnace was raised to 800° C in 7 h (50° C in 1/2 h), and was left at that temperature overnight. The next day they were heated up to 1050° C at the same heating rate, and soaked overnight. They were then cooled to 150° C in 8 h, removed from the furnace at that temperature and stored in a dessicator. At this stage the loss on firing only was only 2-3% by weight.

Figures 4.5 and 4.6 show the contrast between the crucibles made with a P^{H} of 1.0 - 1.5 and 5.5 - 6.0, respectively, after prefiring at 1050°C.



Fig. 4.5 Photograph of two typical crucibles cast at a P^{H} of 1.0 - 1.5 and prefired at 1050°C



Fig. 4.6 Photograph of the crucibles cast at P^{H} of 5.5 - 6.0 and prefired at 1050°C

4.8. SINTERING

4.8.1. History

As stated before, the particle size distribution of the powder plays an important role in the final densification of the sintered product. This is because the driving force for sintering is reduction in surface energy. Minor additions to certain oxides may promote or retard sintering rates. Johnson and Curtis (13) reported that a small addition of CaO (0.5 weight %) improved the sintering rate of thoria at 1700°C. They attributed this to the creation of oxygen-ion vacancies due to the CaO addition, which permitted the rapid diffusion of the structural ions. Both surface and bulk diffusion are mechanisms for material transport in the sintering of thoria. It is to be expected that even though the movement of material on the surface is the process involved in filling the pores or crystal growth, the controlling feature may well be the rate of supply of material to the surfaces by solid diffusion. This rapid diffusion of Ca²⁺, Th⁴⁺ and 0^{2-} through the vacancy structure will increase the sintering rate (51).

Harada et al. ⁽⁵²⁾ obtained densities of 95 to 98% of the theoretical density of thoria by compacting its powders at pressures above 20 tsi and final firing at 1500°C

for 24 hours. Kantan et al. (41) reported that sintering of thoria does not effectively start before 1500°C. Finally, the result of Murray et al. (48) revealed that for a size distribution compatible with Andreason's (see § 4.2.1) analysis, one can obtain densities as high as 96.5% of the theoretical density with presintering at 1350°C and soaking for 5 minutes at 1850°C.

Lidster and Bell ⁽²⁶⁾ pressed ThO₂ (Y₂O₃) powders in a metal die at a pressure of 7 tsi. The pellets were then heated at 1100°C for 24 h followed by 24 h at 1250°C. After this firing cycle the pellets were heated for 7 days at 1600°C. They found that a final firing at 2000°C for 4 h improved the density further, and gave pellets of only 2% porosity. Zador ⁽⁴³⁾, and recently Alcock and Stavropolous ⁽⁵³⁾ found it necessary to vacuum sinter the pellets at 2000°C in order to obtain translucent pellets.

A series of definitive studies of the effect of grain size and density on the partial conductivities and transport numbers of sintered compacts has not been made. However, sintered compacts with disconnected voids and about 95% of theoretical density seem to be generally acceptable for most thermodynamic and kinetic studies.⁽⁵⁾
4.8.2. Sintering Furnaces

Attempts to achieve the maximum possible density by firing the crucibles at 2000°C in a vacuum furnace, with Tungsten elements, failed either because of an improper vacuum, or malfunctioning of the furnace. In one case crucibles made from slip A were fired under argon at 1750°C, however, these crucibles became coated with a layer of tungsten oxide.

At this point, it was decided to design a furnace, exploiting the electronic conductivity of Partially Stabilized Zircon (PSZ) at high temperatures.

When coupled properly in an induction unit, PSZ rings preheated to about 1000°C become conductive and can be used as heating elements. The design of such a furnace requires radio-frequency induction units ⁽⁵⁴⁾.

Any attempt in this laboratory, with coil sizes as small as ID = 1-1/2" and as large as ID = 5", using manufactured castable zirconia or rings cut from a PSZ tube, was unsuccessful. The induction units used were a TOCCOTRON unit with 3000 CPS and 300 KW, or 40,000 CPS and 10 KW. These frequencies were inadequate to provide successful coupling.

Fortunately, with the improvements of slip quality, the final set of crucibles could be fired in an air-oxygengas furnace (Bickley Model 1800 PCE, serial No. 898) with an automatic heating rate and temperature control. After starting the furnace a temperature of 900°C was reached in about 1 h, above this temperature the heating rate could be controlled through a Leeds and Northrup, Model R recorder, which used a radiation pyrometer, aligned with the crucible side.

Any desired heating rate could be programmed on a circular chart associated with the controller.

4.8.3. Sintering of YDT Crucibles

Since the literature study on pure thoria and doped refractory oxides indicated a sufficiently high density by sintering at 1800 - 1850°C, this temperature was chosen as the final sintering temperature.

The prefired crucibles were placed in the hearth of the oxygen gas furnace. Each crucible rested on thoria powder placed on a PSZ tile. After firing for about one hour the gas flow was set on automatic and firing continued. Tables 4.7 and 4.8 show the two different cycles and rates used for small and large crucibles. Out of several heating cycles tried, the ones shown in Tables 4.7 and 4.8 were the most successful.

TABLE 4.7

PROGRAM FOR SINTERING OF SMALL YDT CRUCIBLES

Start program	at 900°C	
Hold program	at 900°C 1	for 1 h
Increase program	to 1850°C	in 6-1/3 h (150°C/h)
Hold program	at 1850°C	for 1/2 h
Decrease program	to 1800°C	in 1/2 h
Hold program	at 1800°C	for 5 h
Decrease program	to 1350°C	in 3 h (150°C/h)
Stop program	at 1350°C	
Leave the furnace	covered until	the next day.

TABLE 4.8

PROGRAM FOR SINTERING OF LARGER YDT CRUCIBLES

Start program	at 900°C
Hold program	at 900°C for 1 h
Increase program	to 1350°C in 3 h
Hold program	at 1350°C for 1 h
Increase program	to 1850°C in 5 h (100°C/h)
Hold program	at 1850°C for 1 h
Decrease program	to 1800°C in 1/2 h
Hold program	at 1800°C for 5 h
Decrease program	to 1350°C in 3 h
Stop program.	•

4.9. PHYSICAL AND MECHANICAL PROPERTIES OF THE CRUCIBLES

After sintering, the crucibles were dense, shiny and orange colored; characteristic of overoxidized thoria. In order to restore the stoichiometry, they were heated in a resistance furnace at 1000°C for about 5 h, under a gas mixture of $p_{H_2}/p_{H_2O} = 1$. After this treatment the crucibles were pure white with some translucency at the edges, and had shrunk 30%, making the total shrinkage about 33% of their dimensions in the mold.

As mentioned earlier, the X-ray diffraction patterns of the YDT (90:10 molar ratio) solid solution gave a lattice parameter a = 5.57 Å. Based on a fluorite type of structure for the solid solution of Y_2O_3 in ThO₂, and the above lattice constant, the X-ray diffraction density of this electrolyte is calculated to be 9.16 g-cm⁻³. The density of the crucibles ranged from 8.68 to 8.80 g-cm⁻³, corresponding to 95 to 96% of the theoretical density.

The crucibles had good thermal shock resistance, and did not crack under heating rates of up to 250°C/h. Liquid iron vanadium melts did not wet these crucibles at 1600°C, and the solidified metal could be shaken out of the crucibles at room temperature. They performed satisfactorily at temperatures of 1550 - 1650°C for long periods of time (6-8 h), as long as they were not cooled to low temperatures.

4.10. ELECTROLYTIC PROPERTIES

In order to check the Electrolytic performance of the crucibles, pieces of 2-3 mm. thick pellets were cut from some of the crucibles with a diamond saw. These pellets were polished and used to find the free energy of formation of Cu₂O and CoO oxides with Ni-NiO reference electrodes, and the values obtained are compared with the literature values.

The cell assembly used for this purpose was shown in Fig. 3.5, and was basically the same as that used by Kiukkola and Wagner $^{(4)}$ and Kontopolous $^{(13)}$. The results of these experiments are presented in Tables 4.9 and 4.10 and in Fig. 4.7. Comparison of these results indicated that the YDT electrolytes were satisfactory at temperatures of 700 - 1100°C.

TABLE 4.9

FREE ENERGY OF FORMATION OF Cu₂O, USING A CELL ARRANGEMENT: Pt|Ni-NiO|YDT|Cu-Cu₂O|Pt

Run	Temp (°K)	E _{Cell} (mV)*	ΔG_{f}° of Cu_{2}^{O} (Kcalmole ⁻¹)
10	1177	255	-20.05
10	1201	244	-20.06
10	1239	235	-20.00
10	1275	230	-19.07
10	1298	230	-19.02
10	1322	233	-18.04

TABLE 4.10

FREE ENERGY OF FORMATION OF COO, USING A CELL

ARRANGEMENT: Pt Ni-NiO YDT CO-COO Pt

Run	Temp (°K)	ECell (mV)*	ΔG_{f}° of CoO (Kcalmole ⁻¹)
14	1183	78.5	-35.79
14	1239	81.0	-34.72
14	1291	87.0	-33.95
14	1335	91.0	-33.29
14	1359	92.0	-32.83

* Each value is the average of two cell EMF with 30 min.
intervals. The readings only varied with ±1 mV.





CHAPTER 5

APPARATUS

The apparatus used in this work was basically the same as that of Kontopolous ⁽¹³⁾, for determining the thermodynamics of liquid Fe-V-O alloys, with some minor adjustments.

5.1. GAS TRAIN

The gas train is shown schematically in Fig. 5.1. The H_2/H_2O mixtures were produced in a constant temperature water bath. Commercial purity H_2 was passed, at room temperature, through a palladium catalyst to convert traces of O_2 to H_2O , then through ascarite to remove CO_2 . After passing through a calibrated flow meter, it was then bubbled through the presaturator and saturators. The presaturator consisted of a flask filled with distilled water and was usually held at a temperature about 20°C higher than the saturators. The saturators consisted of eight flasks connected in series and immersed in a water bath using heavy lead rings. The first seven flasks were filled with distilled water and the last one was empty. The temperature of the water bath was controlled by an immersion resistance heater,



FIG. 5.1 The Gas Train.

which also maintained the water in constant circulation. When H₂ was to be flushed through the furnace, the water bath was bypassed just before the presaturator, by means of a three-way valve, and the H2-line directly joined the argon line near the top of the furnace. Argon was passed through silica gel and "drierite" to remove H₂O, ascarite to remove CO2 and magnesium perchlorate to remove the last traces of H₂O. After going through a calibrated flow meter, the argon was passed over copper-turnings and zirconium-chips held at 670°C, in a resistance furnace, to remove traces of The line pressure was measured by a dibutyl phthalate 0,. manometer. The gas lines from the presaturator to the saturator and from the saturator to the furnace were made of 1/4" OD copper tubing and were heated by means of thermal tape to 80°C, in order to avoid condensation of water vapor.

5.2. THE FURNACE

A vertical, molybdenum wound, tubular resistance furnace was used, for high temperature oxidation-deoxidation studies, in this work. This furnace was the same as that used by Kontopolous ⁽¹³⁾. The furnace and temperature controller assembly are shown schematically in Fig. 5.2.

The furnace tube was high purity recrystallized alumina which was differentially wound with 0.050 in. Mo wire over 10 in. with 10, 9, 8, 9 and 10 turns/in. over 1-1/2, 1-1/2, 4, 1-1/2 and 1-1/2 in. lengths respectively. This differential winding gave a longer furnace hot zone. The furnace tube was centrally located in a brick-lined cylindrical steel shell, 16 in. in diameter and 20 in. in height. The shell was fitted with a removable top to which a 5 in. long extension of 3 in. diameter stainless steel flexible bellows was centrally welded. The purpose of the bellows was to allow for the thermal expansion of the furnace tube. The tube was secured by means of water-cooled glands and "O" rings, located at the base of the shell and at the upper end of the bellows. In this way the shell was made gas tight. The space inside the shell around the tube was filled with -8 + 72 mesh alundum bubbles. A slightly reducing 5% H₂ - 95% N₂ gas mixture was passed through the shell to prevent the Mo-wire from oxidizing.



Fig. 5.2 The furnace and crucible assembly (not to scale).

A Pt+5% Rh - Pt+20% Rh control thermocouple was placed inside a thin recrystallized alumina sheath located at the side of the shell, extending into the hot zone of the furnace tube.

Power to the furnace was supplied through a proportional power controller (Barber-Coleman, series 621) driven by a null balance millivoltmeter controller (Barber-Coleman, model 377D) which received the output from the control thermocouple. A current limiting feature was incorporated in the power controller to limit the output current to a predetermined value. This is essential under load conditions where transformer coupled heating elements have a very low resistance when cold, and a very high resistance when hot, as is the case when molybdenum is used as the resistor element ⁽¹³⁾.

A recrystallized alumina working tube was placed concentrically inside the furnace tube.

A typical temperature profile of the furnace is shown in Fig. 5.3. The temperature variation at the hot zone of the furnace was $\pm 2^{\circ}$ C over 1 in. and $\pm 7^{\circ}$ C over 2 in.

The power controller limited variations in the furnace temperature to ±2°C.





5.3. THE WORKING TUBE AND CRUCIBLE ASSEMBLY

The working tube and crucible assembly are shown in Fig. 5.2. The working tube was fitted with water-cooled brass heads, at the top and bottom, that were sealed with "O" ring seals onto the tube. The head, at the top, had an opening for insertion of a thermocouple sheath, which could also be used for probe insertion; a second opening through which an alumina tube led incoming gas to about 1"-2" above the surface of the melt. A third opening was fitted with an optical flat so that the melt could be observed visually, and a fourth opening served both as a lead wire or sampling port. The head at the bottom was fitted with a gas outlet and with a central opening through which a closed end alumina tube with an alumina cap was inserted to support the crucible. A third opening was used as a second lead wire port.

5.4. MATERIALS

Armco iron and Derby iron were used for most of the experiments. The vanadium was supplied in powder form by Alfa Inorganics. Typical analysis of these materials are given in Tables 5.1, 5.2 and 5.3.

The refractory materials used for the furnace, working and gas inlet tubes, were of high purity recrystallized alumina (McDanel 997). Morganite Triangle RR was used for the crucibles and the thermocouple sheaths.

TABLE 5.1

ANALYSIS OF ARMCO IRON IN w/O

С	Mn	Р	S	Si	Cu	0
		•.				~
0.027	0.045	0.006	0.013	0.000	0.01	0.06

TABLE 5.2

ANALYSIS OF DERBY IRON IN w/O

С	Mn	P	· S	Si	Cu	0
0.005	0.0028	0.001	0.003	0.004	0.0054	0.002

TABLE 5.3

ANALYSIS OF VANADIUM IN ppm (13)

Fe	Si	Al	С	Cr	Others
1000	800	200	900	600	100

5.5. OXYPROBES

The probes used in this work were of the U.S.S. type (3.2.3.4.2), i.e., the CSZ electrolytes were in the form of small cylindrical pellets sealed at the end of a vycor tube.

These pellets, 3 mm in diameter and 6 mm in height, presealed into a 25 mm long by 6 mm OD vycor tube, were supplied by Leigh Instruments Ltd. The vycor tube was extended to 24 in. in length using, either vycor or quartz. The tubes were packed with a mixture of $\text{Cr-Cr}_2\text{O}_3$ powder (90/10 by weight) which acted as the reference electrode. Contact with the electrolyte was made through a molybdenum wire of 0.050 in. diameter. After the molybdenum wire was placed in position, the vycor or quartz tube was sealed under vacuum. Figure 5.4 shows an oxygen probe before and after use.

Contact with the melt was also made with molybdenum wire in order to avoid a thermal EMF correction.

Probes of somewhat different designs were used to measure the oxygen level of the argon gas. Figure 5.5 shows two such cell designs. 0.020 in. Pt wire was used as the contact wire and a Pt + 13% Rh wire facilitated the measurement of temperature at the tip of the probe.



Fig. 5.4 Photograph of the oxyprobes in the original 2.5 cm tips, extended, and used form



Fig. 5.5 Schematic representation of oxyprobes used to find the oxygen content of gases, and temperature, simultaneously

5.6. YDT OXYCELL ASSEMBLY

YDT crucibles were used to design a cell which could continuously monitor the oxygen content of the melt. This cell is shown in Fig. 5.6 and was made by packing a 4:1 $Cr:Cr_2O_3$ mixture (weight) between the YDT crucible and an alumina crucible. The metal-metal oxide served as the reference electrode and was separated from the outside atmosphere by a thick layer of alumina cement. The molybdenum was introduced into the mixture through a 0.050 in. hole in the alumina crucible.



Fig. 5.6 Oxycell assembly

CHAPTER 6

EXPERIMENTAL PROCEDURE

The experiments performed can be divided into two categories. Those performed using "oxyprobes", and those using YDT "oxycells".

6.1. EXPERIMENTS WITH THE OXYPROBES

At the beginning of an experiment the crucible, containing about 100 - 110 g of metal, was placed into the bottom furnace head. After the head was fixed in position, the crucible was pushed upward to the hot zone of the furnace at the rate of about 1 in. per 10 minutes to avoid thermal shock. In the absence of controlled atmosphere the furnace was continuously flushed with purified argon gas.

After the crucible was into position the temperature was raised from 1200°C to the desired experimental temperature. 1200°C was the temperature at which the furnace was held between experiments. This technique gave a longer tube life.

In the Fe-O system, the heat was melted under a continuous flow of purified argon. In this case, the behaviour of the "oxyprobes" was checked and the melt was oxidized with the addition of Fe_2O_3 pellets, and deoxidized with H_2 gas. The oxygen level of the purified argon gas was checked periodically using the modified probe, designed for this purpose. In FeO melts where addition of Fe_2O_3 was made, no sampling or probing was carried out for at least 1-2 h subsequent to any addition, in order to ensure the attainment of equilibrium.

Suction samples were taken from the melt with a transparent quartz tube (3 mm ID). They were removed quickly from the furnace, quenched in liquid nitrogen and stored in a dessicator for analysis. Oxygen was analyzed by inert gas fusion. In all cases, temperature was measured with Pt + 5% Rh - Pt + 20% Rh or Pt - Pt + 13% Rh thermocouples placed in the crucible supporting tube. A periodic check was made by dipping an extended quartz thermocouple sheath into the melt form the top head of the furnace. The two temperatures always agreed within $\pm 3^{\circ}$ C.

Probes were left about 4 to 8 cm above the melt for a few minutes before dipping into the melt, in order to prevent thermal shock. Contact between the probe silica tube and the alumina crucible was avoided in order to eliminate high temperature interaction. It was found that when electrical contact was made at the side of the alumina crucible, where there was usually some oxide, less molybdenum was dissolved. Molybdenum wire was only contacted with the melt when readings were taken with a Croydon potentiometer (type 3), after inserting both probes and molybdenum wire into the melt. No effect was noticed on the EMF readings, with the furnace power switch in "on" or "off" position, indicating that the furnace current had no interaction. No probe failure was encountered at 1550 but apparently one out of four or five probes failed above 1600°C. The probe failure occurred either because of a poor seal around the electrolyte or cracking of the pellets just before dipping into the melt, or both. In either case contact was established between the melt and the reference electrode, resulting in a zero EMF.

Reversibility of the probes was checked by either setting the potentiometer reading about 10 - 20 mV higher or lower than the equilibrium EMF, and closing the circuit for a few seconds, or by passing a small current in either direction by means of a DC supply. Readings which did not come back to the EMF observed before disturbing, or were constantly increasing or decreasing with time were discounted.

For melts in the Fe-V-O system, the procedure was similar to that given above, with the exception that no samples were taken for analysis and oxidation of the melt was carried out by H_2/H_2O equilibration. In these experiments, the occurance of the "transition plateau" was to be detected during deoxidation or oxidation. Thus probing had to be done

at intervals. About 150 g of Armco or Electrolytic iron was placed in an alumina crucible, and vanadium powder was added to give melts of 2, 1 or 0.5% V. In melts containing 2% V the solid oxide cover made it difficult, and sometimes impossible, to insert a probe into the melt. Thus 1 or 0.5% V melts were preferred for most of the experiments.

After the melt was at the experimental temperature, the H₂/H₂O gas mixture was directed to the working tube and oxidation carried out for at least one hour. Oxidation was ensured by the complete coverage of the melt surface with The argon and H₂ gas flow rates were normally kept oxide. at 300 ml/min., i.e., a 1:1 ratio. After sufficient oxidation, the H_2/H_2O gas mixture was replaced by a 80 - 100 ml/min. H₂ flow, and probes were dipped into the melt in 10 to 20 minute intervals and the decrease in oxygen level recorded. The probes were left in the melt for approximately 1-2 minutes, though a constant reading within ±2 mV was achieved after about 10 seconds. A reversibility test was normally carried out after 3 or 4 probe measurements. In cases when the probe reading was not very stable, a second probe was inserted immediately after withdrawal of the first. Some probes were left in the melt for 10 or 20 minutes and gave a constant EMF.

Judging from the length of the molybdenum wire consumed, it was calculated that about 0.2 - 0.3% Mo dissolved in Fe-V-O melts. This amount has a negligible effect on the

activity of oxygen ^(18,73). The dissolution of molybdenum was partially decreased by making the contact with the melt at a spot where oxide had formed. Though no attempt was made to make the contact through a molybdenum-cement cylinder, this may be a solution to the problem of Mo-dissolution.

In some cases, measurements were carried out during oxidation and deoxidation cycles. Each experimental run took from 6 to 8 hours and after each experiment the furnace was cooled down to 1200°C and the crucible removed.

6.2. EXPERIMENTS WITH YDT OXYCELLS

The crucible assembly described earlier (§ 5.7) was used for these experiments. This assembly facilitated a continuous monitoring of oxygen activity during oxidation or deoxidation of Fe-V-O melts. The procedure was basically the same as in the oxyprobe experiments. About 6-8 g of Fe - 0.5% V alloy, previously made by argon arc melting . Derby iron and vanadium powder, was placed in the YDT crucible. The oxycell was then placed in the working tube and pushed up into the hot zone, under argon, at a rate of 1 in. per 10 minutes. When the charge was molten, the argon was replaced with a 4:1 Ar:H, gas mixture. After about 1 h the surface was clear and no oxide film could be detected. At this point oxidation of the melt was carried out, either by "pumping oxygen" to the melt by passing current through the cell or by passing H_2/H_2O gas mixture through the working tube. Deoxidation was carried out using hydrogen or by short circuiting the cell. Normally, when extensive oxidation or deoxidation was to take place, H2/H20 gas mixtures were preferred in order to avoid possible polarization (56) and molybdenum dissolution.

Readings were taken at 1 to 5 minute intervals, depending on the rate of oxidation or deoxidation. In some

cases, readings were taken in both directions, i.e., during oxidation and deoxidation, but in most cases the melt was oxidized first and readings were then taken when deoxidation started. In order to take an EMF reading, the potentiometer was adjusted close to the expected value, molybdenum wire was lowered just to touch the melt, and readings were taken after 5 - 10 sec. The molybdenum wire was then removed from the melt and held above the surface. This procedure gave EMF readings within ±3 mV. A greater accuracy of ±1 mV was possible, if the potentiometer was balanced with taking one's time at the cost of dissolving more molybdenum.

Occasionally, during oxidation or deoxidation, particularly when readings were constant with time, a small potential of about $\pm 20 - \pm 30$ mV was applied. In most cases the readings returned to the equilibrium value in a few minutes, indicating that the system was reversible. In some cases, even an EMF of ± 10 mV did not return to the equilibrium value. The readings in these latter cases always approached a zero EMF upon leaving the cell overnight. When the crucibles were removed, it was noticed that either the molten metal had penetrated the crucible, or green $\text{Cr}_2^0_3$ was present at the electrode-electrolyte interface.

CHAPTER 7

EXPERIMENTAL RESULTS

7.1. CALIBRATION OF THE CSZ OXYPROBES

The performance of the CSZ oxyprobes was checked using Fe-O melts and CO/CO₂ gas mixtures.

(A) Calibration versus Fe-O System: In this system, analyzed oxygen contents were compared with those calculated from cell EMF measurements. The oxygen content was increased by the addition of Fe_2O_3 and sampling was carried out just before probing.

In all cases the probes were investigated for any possible crack in the tube or the CSZ lip after withdrawal from the melt.

Ordinarily more than one probe was used at the same activity of oxygen in the melt, and the EMF readings agreed within ±3 mV.

Table 7.1 and Fig. 7.1A show the results obtained by taking the Henrian activity of oxygen equal to its weight percent, and using Eq. (2.50).

These results indicated that the oxyprobes were performing satisfactorily at 1600°C in the Fe-O melt. The scatter in Fig. 7.1A may be partially due to the uncertainty in the oxygen analysis (±10% of the reported value).

TABLE 7.1

EXPERIMENT IN Fe-O SYSTEM

Run	EMF [mV]	[0] ppm	[0] ppm
		Calculated	Analyzed
l	190	228	238
1	209	280	337
1	245	420	477
2	285	715	706
2	295	750	817
2	300	880	721
2	322	1150	1241
2	345	1650	1585
3	95	69	73
3	110	83	75
3	65	47	54





Similar results are obtained by Fruehan et al. (17) and Kontopolous (13). In Fig. 7.1A a comparison is also made with some of the results obtained by Kontopolous (13) in this laboratory under similar conditions.

(B) Calibration versus CO/CO₂ Gas Mixtures: In this experiment two different CO/CO₂ gas mixtures were used

i)
$$(p_{CO_2}/p_{CO})_a = 15.8 \times 10^{-2}$$

ii)
$$(p_{CO_2}/p_{CO})_b = 11.03 \times 10^{-2}$$

and the probes were of the modified type, as described earlier (§ 5.5.). The cell arrangement may be written as

Pt
$$| Cr-Cr_2O_3 | CSZ | (P_{O_2})_{Ar}, or (P_{O_2})_{CO/CO_2} | Pt$$
. (IX)

The cell reaction is:

$$\frac{4}{3} \operatorname{Cr}(S) + O_2(g) = \frac{2}{3} \operatorname{Cr}_2 O_3(S)$$
(7.1)

and the Gibbs free energy associated with it is

$$\Delta G_{(7.1)} = \Delta G^{\circ}_{(7.1)} - 2.3 \text{ RT log } P_{O_2}$$
$$= -n E_{cell} F$$

(7.2)

where p_0 is the equilibrium partial pressure of oxygen in 2 the gas mixture.

Solving Eq. (7.2) for log po:

$$\log p_{0_2} = \frac{4EF}{4.575 T} + \frac{\Delta G^{\circ}(7.1)}{4.575 T} . \qquad (7.3)$$

Log p_O values calculated from Eq. (7.3) corresponding to 2 different measured cell EMF's are compared in Table 7.2 and Fig. 7.1B with those calculated using the data given in Ref. (69).

As shown in Table 7.2 and Fig. 7.1B, good agreement is indicated for 1600 and 1144°C, but the agreement becomes very poor at 1035°C.

(C) Calibration versus an Applied Potential: (Calibration of Oxyprobes and YDT Oxycell): This method, which seems to be the easiest, was originally suggested by Rapp ⁽⁵⁴⁾, and is based on the principle outlined in Section 2.2.1. In order to carry out this calibration, the YDT oxycell assembly was used with a Fe-Mo-O melt. Molybdenum was added by keeping the lead wire in the melt so long as no more molybdenum dissolved. This prevented further dissolution of the lead wire, and the molybdenum wire could be held in the melt while the potential was being applied through a variable DC source. The diagram shown in Fig. 7.2 represents the technique involved.





TABLE 7.2

CALIBRATION OF CSZ OXYPROBES VS CO/CO2 GAS MIXTURES

Run	Atmosphere	Temp (°C)	EMF (mV)	-log p ₀ measured	-log p ₀₂ calculated
4	Argon	1600	285	9.04	
5	Argon	1144	710	9.15	
•	co/co ₂				
6	mix. (a)	1600	345 344	8.398 8.405	8.313
6	mix. (b)	1600	322 319	8.636 8.669	8.629
7	mix. (a)	1144	399	13.24	13.318
8	mix. (a)	1035	425	14.629	13.03

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Fig. 7.2 Schematic representation of the electrical connection for calibrating the oxyprobe and the oxycell.
Prior to applying any voltage, the melt was deoxidized with purified hydrogen gas, for about 1 h, after which the oxycell gave a reading of 5 mV. At this stage, connections B and C were connected and a set constant voltage was applied for 10 - 12 minutes. At this time a CSZ oxyprobe was inserted and its potential was measured by a potentiometer at port #1, under open circuit conditions, and the two values, i.e., E_{pot} , and E_{appl} , were compared.

Table 7.3 gives the comparison between the applied potentials and the potentiometric readings at 1550°C.

In order to check the performance of the YDT oxycell itself, after the oxyprobe was removed from the melt, connections B and C were disconnected, and potentiometric readings were taken for the oxycell at the port #2, with A connected. Table 7.4 compares the results of such findings.

Since the steady state is achieved in a few minutes ⁽⁶¹⁾, the applied voltage fixes the potential across the YDT oxycell (see § 2.2.1.). Thus the results shown in Tables 7.3 and 7.4 indicate that the oxyprobes used here are only ionic conductors for oxygen activities above $h_0 = 0.0019$, and the YDT oxycell behaved virtually ionically for the whole range ($h_0 = 0.0015$ to $h_0 = 0.0088$) investigated. The reference electrode used in oxyprobes and oxycells is a $Cr(S)-Cr_2O_3(S)$ mixture.

The lower limit of the oxygen partial pressure, at which onset of electronic conductivity at 1550°C occurs in

TABLE 7.3

COMPARISON BETWEEN THE APPLIED VOLTAGE AND THAT OBSERVED BY INSERTING AN OXYPROBE

AT 1550°C

	Applied	Measured	h. corresponding
Run	Voltage	Voltage	
	Eappl.' ^{mV}	Eoxyprobe' ^{mV}	LO Pappl.
9	10	reading unstable	0.0015
9	30	26	0.0019
9	45	43	0.0023
9	100	99	0.0043
9	150	148.5	0.0088

TABLE 7.4

COMPARISON BETWEEN THE APPLIED VOLTAGE

AND THAT OBSERVED BY THE OXYCELL

AT 1550°C

	Applied	Measured	b correctording
Run	Voltage	Voltage	
	Eappl.' ^{mV}	Eoxycell' ^{mV}	to Fappl.
9	10	9.5	0.0015
9	30	28.	0.0019
9	4 5	45.	0.0023
9	100	98.	0.0043
9	150	147.	0.0088

CSZ oxyprobes may be calculated using Eq. (2.7), i.e.,

$$E_{appl.}(I_{ion}=0) = \frac{RT}{4F} \ln \frac{\binom{p_{O_2}}{Fe-Mo-O}}{\binom{p_{O_2}}{(P_{O_2})Cr-Cr_2O_3}}$$
(2.7)

where $(p_0)_{Fe-Mo-O}$ and $(p_0)_{Cr-Cr_2O_3}$ are the equilibrium oxygen partial pressures of the Fe-Mo-O and Cr-Cr_2O_3 systems, respectively.

Solving Eq. (2.7) for $\log(p_0)_{2}$ Fe-Mo-O, one obtains:

$$\log(p_{0_2})_{Fe-MO-O} = \frac{4E_{app1.F}}{2.3 RT} + \log(p_{0_2})_{Cr-Cr_20_3}$$
(7.4)

and using the data given in Ref. (69) one may find $\log(p_0)_{Cr-Cr_2O_3} = -12.54$ at 1550°C. Substitution of this value into Eq. (7.4) gives:

 $p_{O_2} = 6.19 \times 10^{-13}$ atm. at (1550°C) .

$$\log(p_{O_2})_{Fe-MO-O} = -12.208$$

or

7.2. TITRATION OF Fe-V-O MELTS

Following the work of Kontopolous ⁽¹³⁾ and Kay and Kontopolous ⁽⁵⁹⁾, the direct method, outlined in Section 2.2 (p. 39) was used to determine the activity of oxygen at which the transformation of FeV_2O_4 to V_2O_3 , during deoxidation of Fe-V-O melts, takes place.

7.2.1. Titration of Fe-V-O Melts Using CSZ Oxyprobes

In these runs Fe-0.5%V alloys were charged to the furnace and oxidized, at 1600°C, to $h_0 \simeq 0.1$. The melt was then deoxidized with hydrogen gas and the reduction in cell EMF was recorded with time. Tables 7.5, 7.6 and 7.7 give the results obtained using oxyprobes, while deoxidizing with a 100 ml/min. hydrogen flow rate. In Figs. 7.3 and 7.4 these results are plotted as cell EMF versus time for 1600°C.

No probe failure was encountered, and the probe readings were stable with time. They performed satisfactorily as long as they were only used once. When a probe was used twice, the second reading was always 10 - 15 mV lower than the first.

TABLE 7.5

VARIATION OF CELL EMF WITH TIME IN Fe-V-O MELT,

DETERMINED BY CSZ OXYPROBES Run Time (min.) EMF (mV) 15 30

TABLE 7.6

VARIATION OF CELL EMF WITH TIME IN FE-V-O SYSTEM

AT THE TRANSITION POINT Time (min.) EMF (mV) Run . 110 108.5

TABLE 7.7

TRA	NSITION VAI	LUES OF CELI	$E = MF (E^{T})$	AND THE	,
CORRESPOND	ING OXYGEN	ACTIVITIES	(log h_0^T)	IN Fe-V-O	SYSTEM
Run	Temp (°C)	E ^T (mV)	$\log h_0^T$	Scatter (mV)	
15	1600	108	-2.00	±5	
17	1600	107	-2.01	±4.5	









7.2.2. Titration of Fe-0.5%V-O Melts Using YDT Oxycells

In these experiments, the special design of the oxycell assembly made continuous monitoring of the oxygen activity possible. Table 7.8 lists the transition oxygen activities obtained at different temperatures. In Figs. 7.5 through 7.9 the data obtained are plotted as cell EMF versus time. The peaks shown in Figs. 7.5 and 7.9 correspond to the small EMF applied to check the reversibility of It is noticed that the cell EMF always returned the cell. back to the original value. In a few cases when polarization was detected, the EMF approached zero with time with increasing hydrogen flow rate. The duration of the transformation of FeV_2O_4 to V_2O_3 is affected by the hydrogen flow rate; that is, a high flow rate caused a short transition period, and vice-versa.

Figure 7.9 indicates that deoxidation from a level corresponding to $E_{cell} = 220 \text{ mV}$ ($h_0 = 0.032$) did not show any plateau corresponding to other possible transformation involving vanadium oxide with a higher valency state. Although Fig. 7.9 indicates the possibility of a transition of V_2O_3 to a lower vanadium oxide, at E $\approx 20 \text{ mV}$, this could not be substantiated in the present work.

In Table 7.8 a list of transition EMF's and their corresponding oxygen activities, calculated from Eq. (2.5),

TABLE 7.8

TRANSITION EMF AND OXYGEN ACTIVITY IN THE Fe-V-O

SYSTEM USING THE YDT OXYCELL

Run	Temp (°C)	E ^T (mV)	$\log h_0^T$	Scatter (mV)
25	1550	131	-2.05	±2.5
27	1595	116	-2.00	±2.0
30	1600	110	-1.99	±2.0
31	1600	114	-1.96	±2.0
35	1640	141	-1.70	±2.5

TABLE 7.9

COMPARISON OF THE TRANSITION OXYGEN ACTIVITY

WITH THE VALUES IN THE LITERATURE

		Kontopolous	Chipman &Dastur	Narita et al.	Present Work
$\log h_0^T$	(1600°C)	-1.52	-1.4	-1.3	-1.96
$\log h_0^T$	(1650°C)	-1.42		1.17	-1.70*

* Performed at 1640°C

Fig. 7.5 Deoxidation of Fe-V-O system, at 1640°C, using

YDT oxycell



TIME [MIN.] +



Fig. 7.6 Deoxidation of Fe-0.5% V-0 melt at 1550°C, using YDT oxycell

Fig. 7.7 Oxidation of Fe-0.5% V-O melt using YDT oxycell



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Fig. 7.8 Deoxidation of Fe-0.5% V-O system at 1600°C, using YDT oxycell

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Fig. 7.9 Deoxidation of Fe-0.5% V-O melt at 1600°C, using YDT oxycell



are presented. In Table 7.9 (p. 139) a comparison is made between the results obtained in this work and those obtained by different authors at 1600 and 1650°C, respectively.

From Table 7.8 the explicit form of Eq. (2.69) (p. 40) is determined for the variation of log h_{Ω}^{T} with temperature.

$$\log h_0^T(T) = 4.52 - \frac{12000}{T} \pm 0.06$$
 (7.5)

This relationship is shown graphically in Fig. 7.10 and corresponds to the chemical reaction occurring during the transition period, i.e.,

$$FeV_2O_4(S) = V_2O_3(S) + [O]_{1wt} + Fe(l)$$
 (7.6)

The free energy of this transformation is given by

$$\Delta G_{(7,6)}^{\circ} = -2.3 \text{ RT } \log K_{(7,6)} \qquad (7.7)$$

It follows from Eqs. (7.5) and (2.69) that

$$\Delta G_{(7.6)}^{\circ} = 54700 - 20.60T \pm 500 \text{ [cal.]}$$
 (7.8)

In Table 7.10 a comparison is made between the Gibbs free energy relation obtained in the present work and those obtained by different authors.





TABLE 7.10

COMPARISON OF THE FREE ENERGY OF FORMATION FOR THE REACTION						
$FeV_{2}O_{4} = V_{2}O_{3} + [O]_{1wt} + Fe(l)$						
Author	$\Delta G^{\circ}_{(7.6)}$ (Cal.)	ΔG [°] (7.6) ^(1600°C)	Ref.			
Chipman and Dastur (1951) .		+12900	(57)			
Karasev et al. (1952)	40320-17.32 T	+ 7020	(72)			
Narita et al. (1969)	-11100- 0.492T	-12022	(58)			
Kontopolous (1971)	22350- 4.98 T	+13000	(13)			
Present Work (1972)	54700-20.60 T ± 500 [cal.]	+17300	•			

CHAPTER 8

DISCUSSION AND CONCLUSIONS

8.1. PROPERTIES OF YDT AND CSZ ELECTROLYTES

A comparison of the free energies of formation of CoO and Cu₂O obtained by using YDT solid electrolytes, with those compiled by Gleiser and Elliot ⁽⁷⁸⁾ (§ 4.10) indicate a slight deviation of about 0.5 and 1.0 Kcal.-mole⁻¹, respectively. The cell EMF was reproducible within ± 1 mV (± 45 cal.). In view of the uncertainties normally reported in free energy data (± 1 Kcal. for accurate data), and the temperature variation ($\pm 2^{\circ}$ C) in the experiments, this small deviation is reasonable and the YDT electrolyte is assumed to be an ionic conductor in the temperature range 900 -1100°C.

Furthermore, the calibration of YDT crucibles versus an applied voltage at 1550°C indicates that the electrolyte is also behaving ionically at this temperature. The differences shown in Table 7.4 between the applied voltages and the open circuit voltages measured, with YDT oxycell, may be due to the lack of attainment of steady state conditions (see § 2.2.1, p. 8).

Inspection of the oxycell assembly, after use, indicated a reaction between the molybdenum wire and the

 $Cr-Cr_2O_3$ reference electrode, when the assembly was left in the furnace for long times (about 36 hours). No reaction was detected after only 12 hours experimentation.

The electrolytic performance of the oxycell was checked in Fe-O system, assuming that the Henrian activity of oxygen is equal to its weight percent. The agreement between the analyzed oxygen and the percent oxygen calculated from Eq. (2.50) is fairly good, if one considers the uncertainty involved in oxygen analysis by inert gas fusion (±10% of the reported value), and the free energy of formation of Cr₂O₃ (reference electrode). This reasoning can further be substantiated by consideration of the results obtained using CO-CO, gas mixtures. As shown in Fig. 7.1B, as long as the CSZ oxyprobes were used within their ionic domain (onset of electronic conduction = $p_{0_2} \simeq 10^{-13}$ atm.), there was a good agreement between the calculated oxygen partial pressures from Eq. (7.3) and those obtained from the thermodynamic data of Jeannin et al. (69). The good agreement obtained for the CO-CO₂ gas mixture B at 1144°C is not justifiable, since at this temperature, the oxygen partial pressure in equilibrium with both, CO-CO, gas mixture and the Cr-Cr₂0₃ reference electrode are out of the electrolytic This is very likely due to an erroneous EMF recorddomain. ing. The poor agreement obtained at 1035°C is also because of the electrolyte operating outside of its electrolytic At this temperature the oxygen partial pressure in domain.

equilibrium with a $(p_{CO_2}/p_{CO}) = 15.8 \times 10^{-2}$ is about 9.3 × 10⁻¹⁶ atm., and that in equilibrium with $Cr-Cr_2O_3$ is about 10⁻²² atm.

The oxygen partial pressure at which the electronic conductivity of the CSZ used here becomes appreciable at about $p_{0_2} \approx 7 \times 10^{-13}$ atm. at 1550°C. This value is shown in Fig. 3.1 along with others compiled by Patterson ⁽¹¹⁾. While the comparison indicates a compatibility with the result of Fruehan et al. ⁽¹⁷⁾, it is out of the ionic domain proposed by Patterson ⁽¹¹⁾.

Based on the great controversy in the reported electrolytic domain of CSZ and YDT, and the results obtained by Schwerdtfeger⁽¹⁸⁾, Fruehan et al. ⁽¹⁷⁾, Kontopolous ⁽¹³⁾ and this work, one may conclude that the extent of the electrolytic domain of these electrolytes is a strong function of dopant concentration and impurities, and perhaps the type of impurities involved. Thus the probes should always be calibrated before use.

8.2. TRANSITION OF $FeV_2O_4 \rightarrow V_2O_3$

While comparison of Tables 7.7 and 7.8 reveals a good agreement between the results of the oxyprobes and the oxycells, investigation of Table 7.9 indicates relatively high differences between the results obtained by Kontopolous ⁽¹³⁾, Chipman and Dastur ⁽⁵⁷⁾ and Narita et al. ⁽⁵⁸⁾, at all temperatures investigated.

The uncertainties involved in this experiment, $\pm 2^{\circ}$ C in temperature measurements, ± 2 mV in cell EMF and $\pm 200 \text{ cal.-mole}^{-1} \circ_2$ in the free energy of formation of $\operatorname{Cr}_2 \circ_3$ from the data of Jeannin et al. ⁽⁶⁹⁾, do not account for the discrepancy involved. This is more likely due to the difference in the techniques involved. As described earlier (§ 3.1) these authors have all found the transition point by the indirect method, i.e., interpolation of log h₀ vs log h_V data of high and low vanadium contents. This interpolation is associated with uncertainties much larger than those arising from experimental inaccuracies.

Because of the large deviations involved in the reported free energy of formations of FeV_2O_4 and V_2O_4 , and thus in the free energy of formation of the transition reaction (7.6), it is not wise to compare a theoretical value for the transition oxygen activity h_0^T , with that obtained experimentally in the present work.

APPENDIX A

SAFETY PRECAUTIONS IN WORKING

WITH THORIUM COMPOUNDS

Since thorium and most of its compounds are slightly radioactive and poisonous, it is wise to take certain necessary precautions while working with them. The International Atomic Energy Agency ⁽⁴⁶⁾ gives the following information about thoria. One g of Th^{Nat.} contains 0.11 μ Ci²³²Th, 0.11 μ Ci²²⁸Th and various amounts of ²²⁷Th, ²³²Th and ²³⁴Th, depending on the source. Table A.1 gives the maximum permissible intakes of Th^{Nat}. Although calculations and animal experiments suggest that Th^{Nat.}, if ingested intervenously, is perhaps as hazardous as Pu and indicate the values listed in Table A.1, experience to date has shown that in industrial circumstances the hazard of Th^{Nat.} is not much greater than that of U^{Nat.}. Therefore, a yearly intake by inhalation of 6.6 \times 10⁵ µg of Th^{Nat.} for workers directly engaged in radiation work during working hours, is recommended as a provisional level ⁽⁴⁶⁾.

Based on this information and radiation measurements taken here on the materials and solutions used for the preparation of YDT, it is safe to assume that thorium and its various compounds, used here, are more toxic than

TABLE A.1

MAXIMUM PERMISSIBLE INTAKE OF Th^{Nat.}

Radio-	Critical	Workers		Members of the Public	
Nuclide	Organ	Organ content giving the maximum permissible dose-rate (µg)	Maximum permissible annual intake by ingestion (µg)	Limits of annual intake by ingestion (µg)	Limits of annual intake by inhalation (µg)
Th ^{Nat.}					
Soluble	Bone	8.0 \times 10 ⁴	3.7×10^4	9.5 × 10 ⁶	3.7×10^{3}
_	Lung		9.3 × 10^4	-	9.3 × 10^3
Insoluble	GI (LLI) *			7.1 × 10 ⁷	· -

- * GI = Gastro-Intestinal Tract,
 - LLI = Lower Large Intestine.

radioactive*. Therefore, while preparing the proper solutions for thoria, yttria coprecipitation, necessary measures should be taken to avoid contamination of the hands. During grading of the YDT powder, a proper mask should be used to avoid inhalation.

Since thoria is a very heavy oxide (specific gravity = 10), inhalation of a small amount of its dust may exceed the permissible intake level.

* The level of radiation in the case of thorium nitrate, thorium oxalate, and the fired crucibles was less than that of the standard used in the radiation meter.

APPENDIX B

DETERMINATION OF SIZE DISTRIBUTION BY THE METHOD OF ANDREASON-LUNDBERG ⁽⁴⁷⁾

This is the most commonly used technique and is based essentially on the Stokes' law. A suspension is made up in a cylindrical vessel (Fig. B.1) and is then allowed to settle. Samples of the suspension at a fixed distance from the surface are withdrawn by a pipette at suitable intervals.

The graduated cylinder is filled to the level E with a suspension of water and 5 w/0 YDT sample, which is obtained by coning and quartering. HCl is added to the suspension as a dispersant. A 10 ml pipette A is connected through the two way tap B to the stem D, through which liquid can be drawn from the level F, 20 cm below E. The alternative outlet C allows a sample, which has been collected in the pipette, to be transferred to a weighed dish.

Samples are drawn at specific intervals and the concentration at the point F is determined by weighing the dried residue in the collecting dishes.

Each sample collected contains particles of all sizes, from the largest remaining above the level F, to the smallest which was present originally. Particles of one particular size (d_1) will, at the start of the experiment, be distributed



uniformly through the volume of the suspension. They each must fall with the same velocity, hence their concentration around the level F will be constant until all of these particles (d_1) which were at the level F have fallen through 20 cm. No more particles of this size can then be drawn into the pipette on subsequent sampling. Therefore, the overall concentration will be lowered, since only particles less than d_1 will remain in suspension. The velocity of a spherical particle falling through a fluid medium is given by Stokes' law:

$$v = \frac{1}{18} \frac{(\rho_{\rm S} - \rho_{\rm L}) d^2 \times g}{\eta}$$
 (4.2)

Substitution of the appropriate values for constants at 25°C, and replacing v by H/t, will result in:

$$d = 2.5 \times 10^{-3} t^{-1/2}$$
 (4.5)

where d is the diameter in cm and t is the time in minutes. Values of d found from the relation (4.5) do not, however, exactly represent the maximum particle size present in each sample, because every time that a sample of suspension is drawn from the cylinder, the surface of the suspension falls slightly (hence reducing H slightly). Thus the calculated values of d must be corrected by multiplying each one by an appropriate correction factor B, given by

$$B = \frac{[H-x(n-1)]^{1/2}}{H^{1/2}}$$
(B.1)

where H is the initial depth of sampling (20.0 cm), x is the drop in level of the suspension per sample (equals 0.4 cm), and n is the number of the samples. The result of such analysis may be represented as a histogram or as w/0 undersize versus particle diameter.

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