

3. EXPERIMENTAL

3.1. Introduction

Because little information is available on phase relations within the pseudo-ternary system $\text{TiO}_x\text{-FeO}_y\text{-VO}_z$ and because this information is a prerequisite for activity measurements in the system it was decided to make a starting contribution towards determining the necessary phase relation data. Since the phase relation data for the FeO-TiO_2 pseudo-binary system is known to a large extent it was decided to concentrate effort on the remaining two pseudo-binary systems within the pseudo-ternary system, that is the $\text{V}_2\text{O}_3\text{-FeO}$ and $\text{V}_2\text{O}_3\text{-TiO}_2$ pseudo-binary systems.

The experimental technique used to determine phase relations in the two pseudo-binary systems $\text{V}_2\text{O}_3\text{-FeO}$ and $\text{V}_2\text{O}_3\text{-TiO}_2$ was to react the respective samples under specific partial oxygen pressures, and at specific temperatures, until chemical equilibrium was attained. On completion of the reaction period the samples were quenched in water, and subsequently analysed for phase and chemical compositions. The experiments were conducted at 1400°C , 1500°C and 1600°C . The maximum temperature of 1600°C was used because that was the maximum temperature that the furnace could reach comfortably. In order to determine trends in the phase boundaries on the pseudo-binary diagrams the temperatures of 1400°C and 1500°C were chosen as experimental temperatures, in addition to 1600°C .

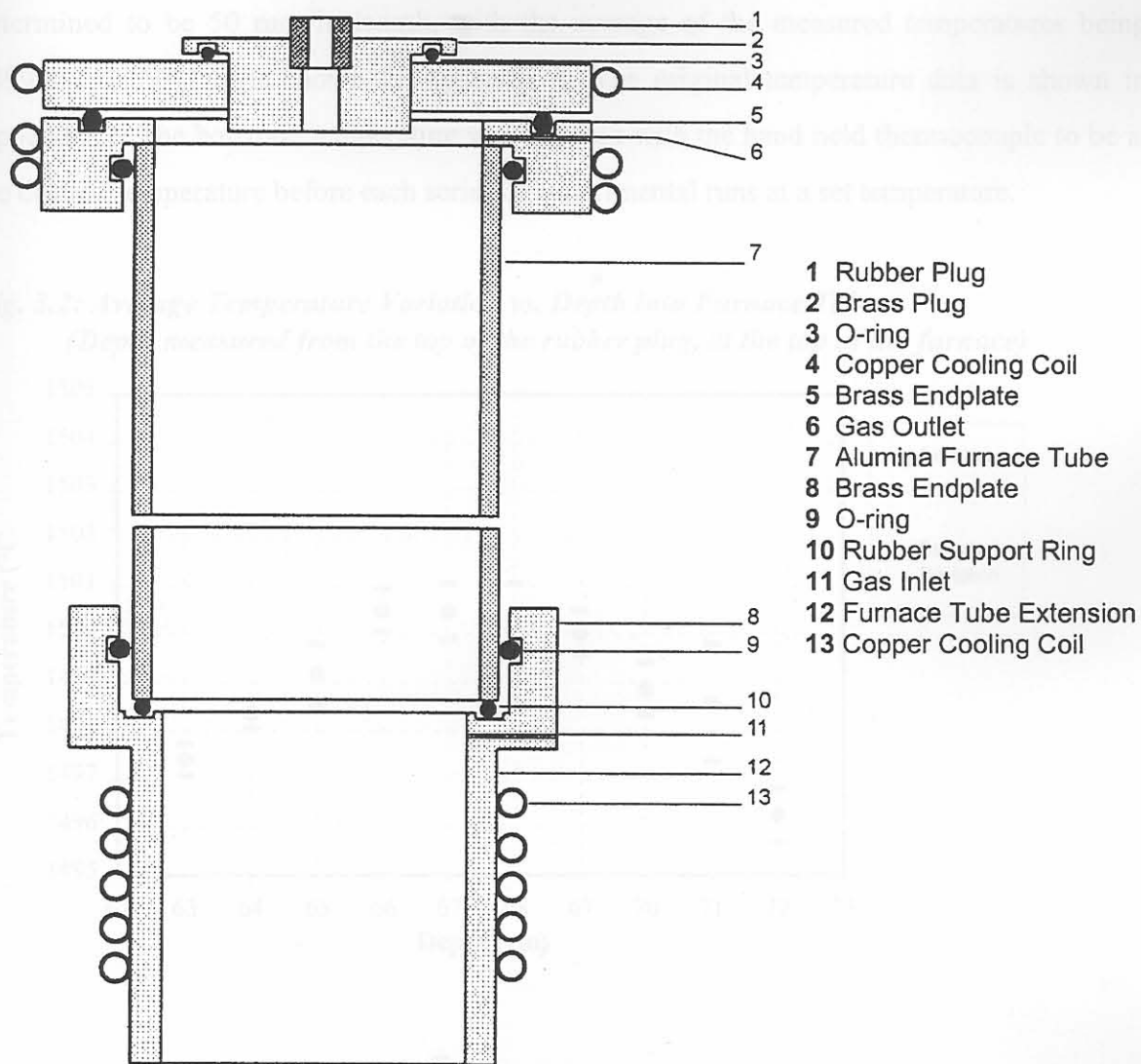
3.2. Experimental Set-up

3.2.1. Furnace Set-up

A schematic representation of the furnace assembly set-up is shown in Fig.3.1. The vertical tube resistance furnace employed six equidistant lanthanum chromite (LaCrO_3) heating elements, situated around the furnace tube, on a circle of a radius of 57.5 mm, measured from the furnace tube centre to the centre of an element. The alumina furnace tube, 99.8% Purity, 88.90 mm O.D. x 79.37 mm I.D. x 1200 mm length, was fitted with water-cooled brass fittings at both ends which were sealed to the tube furnace with O-rings. The top brass fitting contained an O-ring sealed brass plug, through which samples were introduced into the furnace tube. The bottom fitting extended below the alumina furnace tube. The bottom fitting was supported by a steel bracket attached to the furnace framework, which in turn supported the furnace tube. The furnace temperature was controlled by a PID controller/programmer using a Pt-13%Rh/Pt thermocouple which was positioned next to the furnace tube, close to the

hot zone. The exact position of the hot zone in the furnace was established by placing a hand held Pt-13%Rh/Pt thermocouple at various depths into the furnace tube.

Fig.3.1: Furnace Assembly Set-up



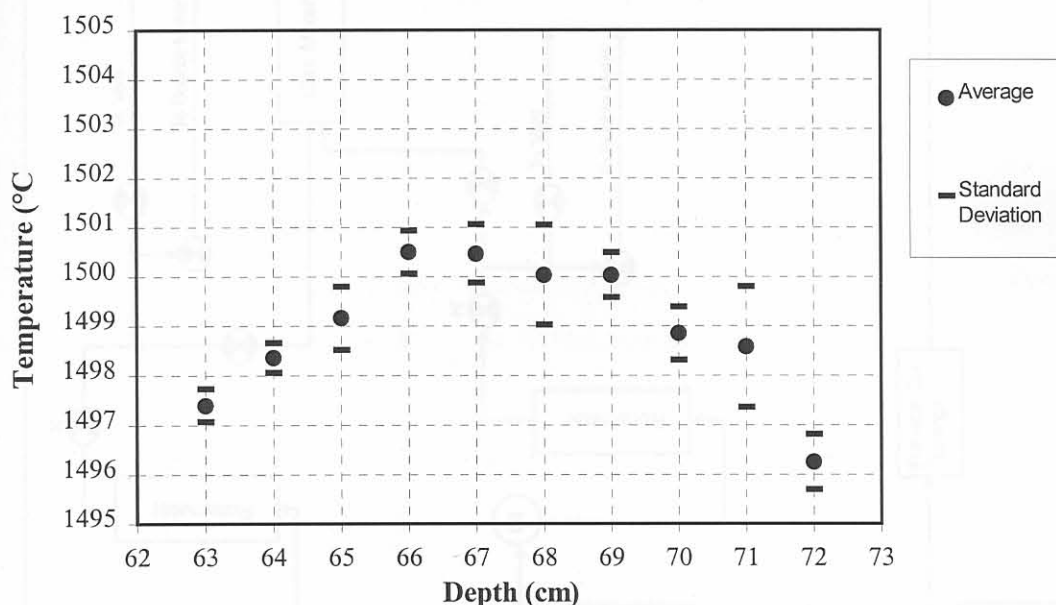
- 1 Rubber Plug
- 2 Brass Plug
- 3 O-ring
- 4 Copper Cooling Coil
- 5 Brass Endplate
- 6 Gas Outlet
- 7 Alumina Furnace Tube
- 8 Brass Endplate
- 9 O-ring
- 10 Rubber Support Ring
- 11 Gas Inlet
- 12 Furnace Tube Extension
- 13 Copper Cooling Coil

3.2.2 Gas System

A specific partial oxygen pressure was maintained within the furnace by mixing CO and CO₂ in specified volumetric proportions at a total flow rate of 0.50 cm³ min⁻¹ at STP, that is a superficial velocity of 0.20 cm/s at STP, with the sectional area of the furnace tube being 25.3 cm². The volumetric proportions required to fix the oxygen partial pressure at a selected temperature were obtained from the tables compiled by Deines et al.¹⁰ In order to control gas flow rates and clean, mix and transport the gases a gas system was constructed from PVC tubing, ball valves and ratchet clamps. Fig. 3.2 shows a schematic representation of the gas system.

The hand held thermocouple was checked against a standard thermocouple which was certified to have a maximum deviation of $\pm 1.003^{\circ}\text{C}$ from the standard for $1100\text{-}1600^{\circ}\text{C}$. The hand held thermocouple measured $1500.21 \pm 0.27^{\circ}\text{C}$ and the standard thermocouple measured $1499.86 \pm 0.26^{\circ}\text{C}$ at the same temperature. The average temperature variation with increasing depth down the furnace tube is shown in Fig. 3.2, at 1500°C . The furnace hot zone was determined to be 50 mm in length, with the average of the measured temperatures being $1499.85 \pm 0.89^{\circ}\text{C}$ as is shown in Appendix 1. The original temperature data is shown in Appendix 2. The hot zone temperature was checked with the hand held thermocouple to be at the desired temperature before each series of experimental runs at a set temperature.

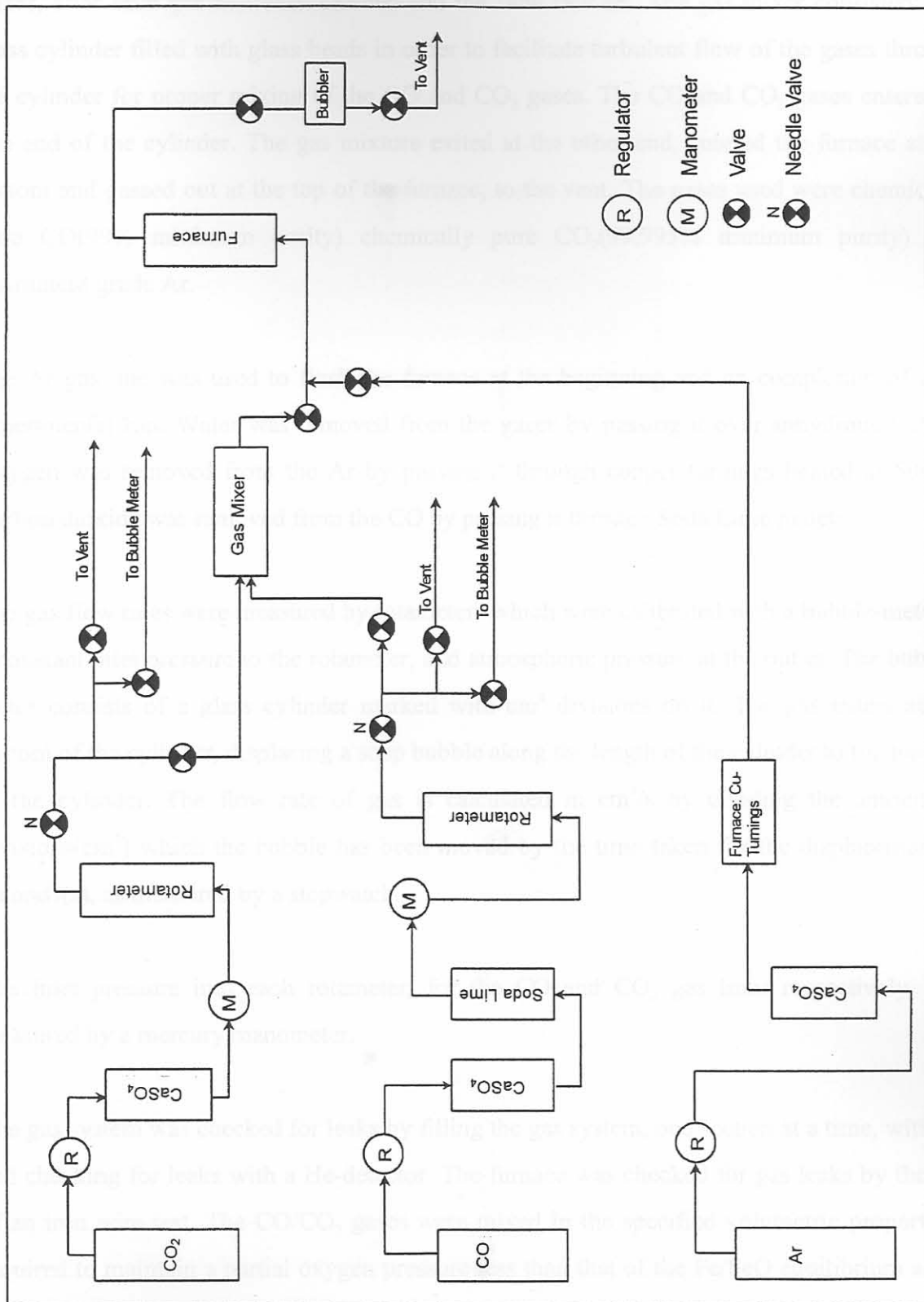
Fig. 3.2: Average Temperature Variation vs. Depth into Furnace Tube
(Depth measured from the top of the rubber plug, at the top of the furnace)



3.2.2. Gas System

A specific partial oxygen pressure was maintained within the furnace by mixing CO and CO₂ in specified volumetric proportions at a total flow rate of 600 cm³/min at STP, that is a superficial velocity of 0.20 cm/s at STP, with the sectional area of the furnace tube being 50.3 cm². The volumetric proportions required to fix the oxygen partial pressure at a selected temperature were obtained from the tables compiled by Deines et. al.¹⁷ In order to control gas flow rates and clean, mix and transport the gases a gas system was constructed from PVC tubing, ball valves and ring clamps. Fig. 3.3 shows a schematic representation of the gas system.

Fig. 3.3: Gas System



The gas system contained two separate gas lines for CO and CO₂, which joined at the gas mixer, after each gas had been cleaned and the flow rate set. The gas mixer consisted of a glass cylinder filled with glass beads in order to facilitate turbulent flow of the gases through the cylinder for proper mixing of the CO and CO₂ gases. The CO and CO₂ gases entered at one end of the cylinder. The gas mixture exited at the other end, entered the furnace at the bottom and passed out at the top of the furnace, to the vent. The gases used were chemically pure CO(99% minimum purity) chemically pure CO₂(99.995% minimum purity) and instrument grade Ar.

The Ar gas line was used to flush the furnace at the beginning and on completion of each experimental run. Water was removed from the gases by passing it over anhydrous CaSO₄. Oxygen was removed from the Ar by passing it through copper turnings heated at 500°C. Carbon dioxide was removed from the CO by passing it through Soda Lime pellets.

The gas flow rates were measured by rotameters which were calibrated with a bubble-meter at a constant inlet pressure to the rotameter, and atmospheric pressure at the outlet. The bubble-meter consists of a glass cylinder marked with cm³ divisions on it. The gas enters at the bottom of the cylinder, displacing a soap bubble along the length of the cylinder to the top end of the cylinder. The flow rate of gas is calculated in cm³/s by dividing the amount of divisions(cm³) which the bubble has been moved by the time taken for the displacement in seconds(s), as measured by a stopwatch.

The inlet pressure into each rotameter, for the CO and CO₂ gas lines respectively, was measured by a mercury manometer.

The gas system was checked for leaks by filling the gas system, one section at a time, with He and checking for leaks with a He-detector. The furnace was checked for gas leaks by the use of an iron wire test. The CO/CO₂ gases were mixed in the specified volumetric proportions required to maintain a partial oxygen pressure less than that of the Fe/FeO equilibrium at the test temperature of 1303°C.¹⁸ An iron wire, 0.9 mm diameter and 99.5% purity, was pushed through an alumina tube with at least 50 mm of iron wire protruding from one end of the tube, and the piece of iron wire protruding from the other end bent through 180°. The tube was sealed with silicone sealant at this end as shown in Fig. 3.4. This iron wire and alumina rod assembly was subjected to the above conditions for 1 hour. The iron wire was pulled up the

alumina rod, leaving the bottom 70 mm in the tube section protruding from the furnace in order for the iron wire to cool down, after which it was removed from the alumina rod. The absence of oxidation products on the iron wire indicated the absence of leaks in the furnace.

The variation in the set partial oxygen pressure was estimated by employing the procedure used in checking the furnace tube for leaks, that is the iron wire test described above. The CO/CO₂ gases were mixed in the specified volumetric proportions required to maintain a partial oxygen pressure 0.5log₁₀ units above and below that of the Fe/FeO equilibrium at the test temperature of 1303°C. The equilibrium partial oxygen pressure (P_{O₂}) for the Fe/FeO equilibrium is 1.91×10^{-11} atm (log P_{O₂} = -10.72 atm) at 1303°C¹⁸. Therefore the partial oxygen pressure was set at 6.03×10^{-12} atm (log P_{O₂} = -11.22 atm) for checking the variation in the set partial oxygen pressure on the Fe side of the Fe/FeO equilibrium, and set at 6.03×10^{-11} atm (log P_{O₂} = -10.22 atm) to check the variation in the set partial oxygen pressure on the FeO side of the Fe/FeO equilibrium, at 1303°C. No oxidation product was observed on the iron wire for the test done at the partial oxygen pressure of 6.03×10^{-12} atm, and wüstite was observed on the iron wire for the test done at 6.03×10^{-11} atm indicating that the variation in the set partial oxygen pressure was within a factor of 10^{0.5} of the Fe/FeO equilibrium partial oxygen pressure at 1303°C.¹⁸

3.2.3. Quenching Set-up

The bottom end of the furnace tube was sealed by a PVC membrane, thickness = 50 µm, wrapped over the furnace tube opening, with a layer of vacuum grease as sealant between the brass tube and the PVC. The PVC was held in place by two rubber bands. The PVC-covered tube end was immersed in water, contained in a bucket through which water was pumped continuously in order to keep the PVC cool.

The quenching rod, shown schematically in Fig. 3.5, consisted of a double bore alumina tube. Molybdenum wire of 1 mm diameter was pushed through each bore and bent at the top. The holes were sealed at the top with silicone sealant. The molybdenum wires protruding from the bottom of the alumina rod were bent to form two hooks. The hooks were bridged by 0.3 mm diameter molybdenum wire. The sample hung from this bridge. To quench the sample, an electrical current was sent through the molybdenum wire circuit via the top connections, and the 0.3 mm diameter molybdenum wire melted whereby the sample was released to fall through the PVC cover and into the water at the bottom of the furnace.

Fig. 3.4: Iron Wire and Alumina Rod Assembly

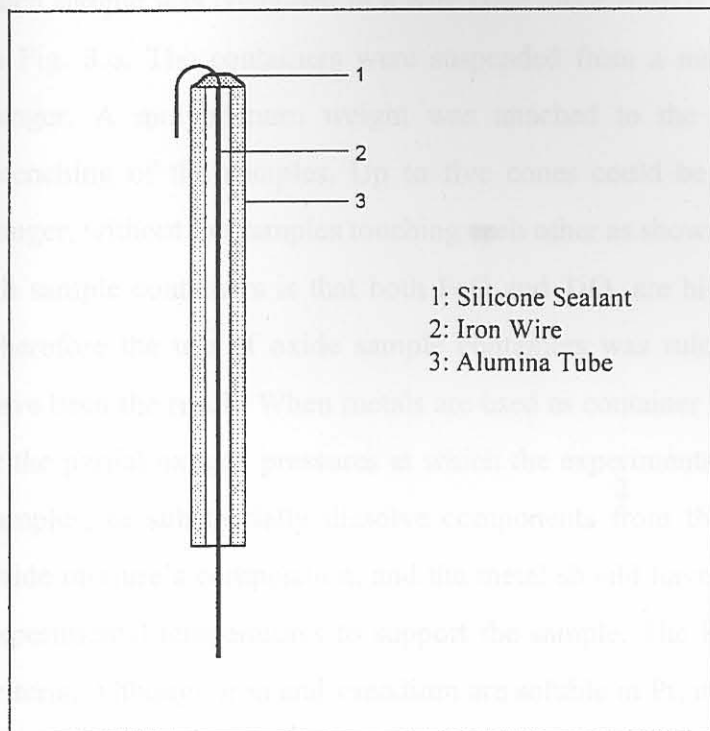
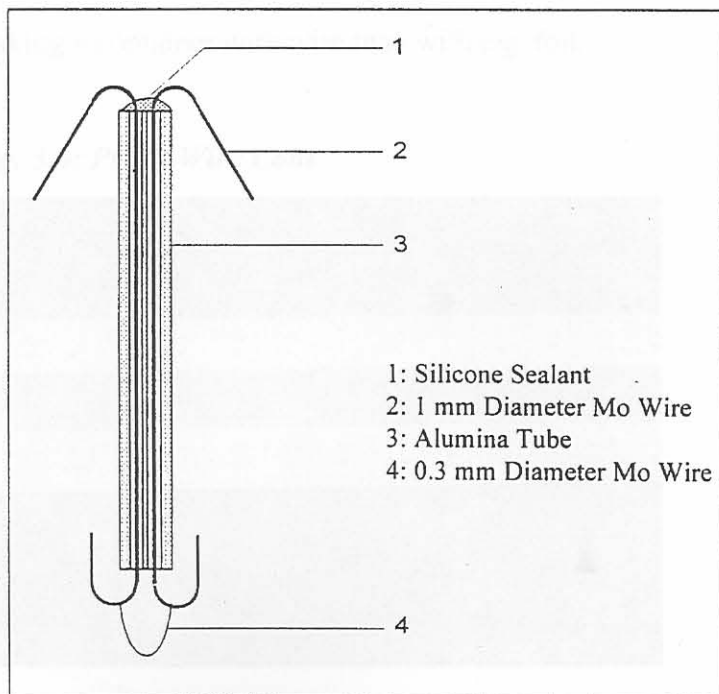


Fig. 3.5: Quenching Rod



3.2.4. Crucibles

Each sample was contained in a wire cone made from 0.5 mm diameter Pt-Rh wire as shown in Fig. 3.6. The containers were suspended from a molybdenum wire bent into a circular hanger. A molybdenum weight was attached to the hanger in order to facilitate rapid quenching of the samples. Up to five cones could be suspended from each molybdenum hanger, without the samples touching each other as shown in Fig. 3.7. The reason for using Pt-Rh sample containers is that both FeO and TiO₂ are highly corrosive towards other oxides. Therefore the use of oxide sample containers was ruled out because contamination would have been the result. When metals are used as container material the metal should not oxidise at the partial oxygen pressures at which the experiments are done, or dissolve into the oxide samples, or substantially dissolve components from the oxide samples and so change the oxide mixture's composition, and the metal should have the required physical strength at the experimental temperatures to support the sample. The Pt and Pt-Rh mixtures satisfied these criteria. Although iron and vanadium are soluble in Pt, it was found that little or no vanadium and iron absorption into the Pt took place. This is most probably due to the partial oxygen pressures used in the experiments being oxidising relative to iron and vanadium. Furthermore, contact between the sample and sample container material was limited because the majority of the reacted samples remained solid throughout the experiments. Sample containers were made from wire to ensure good sample-gas contact, and because less Pt-Rh material is required in making a container with wire than with e.g. foil.

Fig. 3.6: Pt-Rh Wire Cone

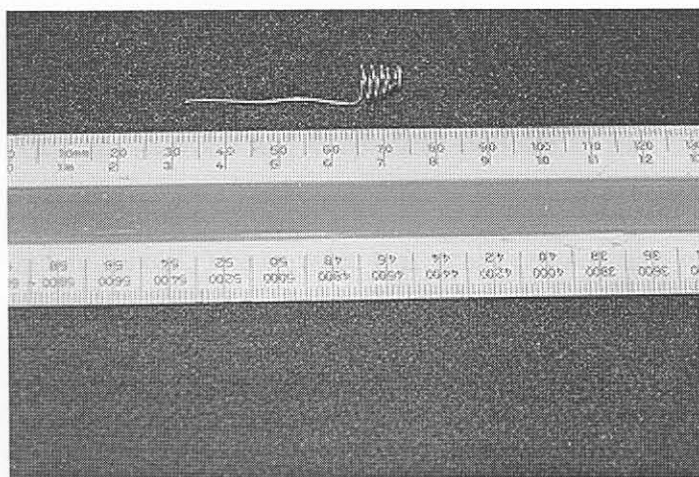
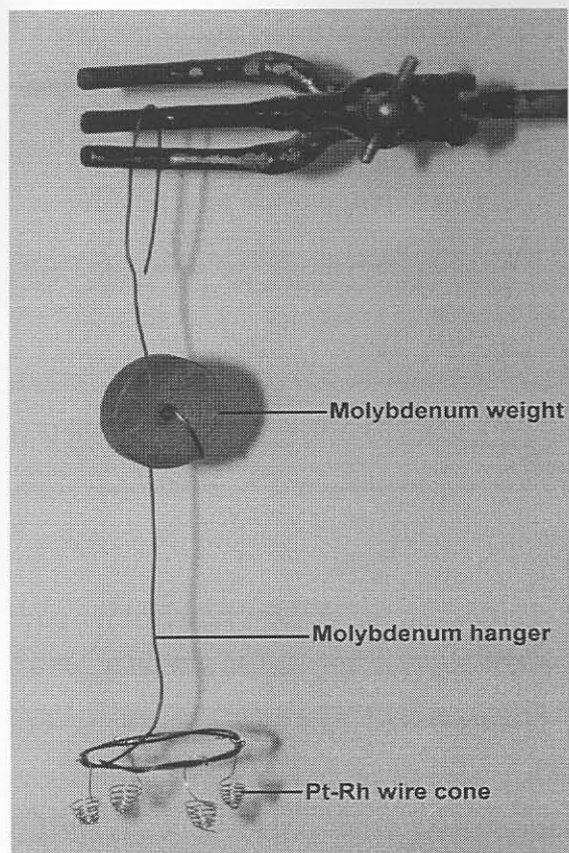


Fig. 3.7: Molybdenum Hanger and Pt-Rh Wire Cones



3.3. Experimental Procedure

3.3.1. Sample Preparation

The following chemicals were used: GP-grade V_2O_5 (Assay: >99%), Fe_2O_3 (Assay: minimum 99%) and extra pure TiO_2 (Assay: 99-100.5%). The powders were dried by heating at $400^\circ C$ for 12 hours and stored in a desiccator. Samples were made up by determining the required mass of powders and mixing these thoroughly under acetone, with a spatula, on a watch-glass. After the acetone had evaporated pellets, 15 mm in diameter and 5-10 mm in height, were pressed from the mixture and these pellets were sintered for 48 hours at $550^\circ C$ in air, crushed and re-mixed. The powder was again pressed into pellets and sintered for another 16 hours. The pellets were stored in a desiccator. The pellets were chipped down to pieces of 0.1-0.2 g which fitted easily into the sample containers to be used in the experiments.

3.3.2. Experimental Run

Before each experiment the furnace was flushed with purified Ar. The desired CO₂ flow rate was set by using the bubble-meter, after which it was bypassed to the vent. The CO flow rate was then fixed in a similar manner, after which it was combined with the CO₂ flow through the bubble-meter for the period of time taken to introduce the sample into the furnace tube, under Ar. The Ar was replaced with the CO/CO₂ gas mixture and the sample was lowered into the hot zone of the furnace. On completion of the reaction period of 24 hours, the sample was quenched in water. The sample was retrieved from the water and the CO/CO₂ gas flow replaced by Ar. After the CO and CO₂ gas was flushed from the furnace, the broken PVC cover was replaced with a new layer of PVC.

3.3.3. Sample Analyses

Phase analyses constituted X-ray diffraction (XRD), Electron probe microanalysis (EPMA)-EDS (Energy Dispersive Spectrometry) and optical microscopy. On completion of each experimental run, part of the sample was milled into powder for XRD analysis. XRD analysis was performed with a Siemens Kristalloflex 810 diffractometer, using Cu K_α radiation. Polished sections were also made from parts of the sample and these were studied under the optical microscope. With the XRD and optical microscopy information in hand, Electron probe microanalyses were done on the polished sections, using a JEOL JXA733 Electron probe microanalyser. Integration of the data from these analysis techniques made phase characterisation of each sample possible.

As an example of the process followed in phase characterisation, the 50 mass% V₂O₅-50 mass% Fe₂O₃ sample reacted for 2.67 hours at 1400°C, for equilibrium time determination purposes, is discussed in detail here. From the XRD pattern, shown in Fig. 3.10, the presence of a crystalline phase with metal and oxygen ions in the co-ordination M₃O₄ is identified. This is indicated by the match between the peaks in the diffraction pattern, and those for the magnetite (Fe₃O₄) standard. From the photomicrograph taken from the polished section, under reflected light, two phases are identified, the main phase which is beige in colour and a secondary phase which is yellow in colour (with an unfiltered tungsten light source). From the following observations it is concluded that one of the phases must be amorphous: only one crystalline phase is indicated on the XRD analysis and a quench structure is observed in the polished section. The EPMA analyses in Table 3.1 indicate that both phases contain iron and vanadium. The EPMA analyses are originally expressed in terms of FeO and V₂O₃ because

the cations expected to exist under the experimental conditions employed are Fe^{2+} and V^{3+} . This information indicates that the sample consists of two phases, a crystalline phase of M_3O_4 co-ordination consisting of 52.69 mass% FeO and 47.31 mass% V_2O_3 , that is 0.73 mol Fe per 0.63 mol V, and a liquid phase consisting of 85.85 mass% FeO and 14.15 mass% V_2O_3 , that is 1.19 mol Fe per 0.19 mol V.

3.3.4. Equilibrium Time Determination

In order to determine the minimum reaction time to establish chemical equilibrium within the samples, one of the initial sample compositions is reacted for increasing periods of time. Equilibrium is considered to have been reached when the number of phases in the sample, the volume fractions of the respective phases and the chemical composition of the respective phases cease to change with a further increase in reaction time. The minimum reaction time required to attain equilibrium throughout the sample is thus indicated by the period of reaction time that was needed for the onset of the stabilisation of the chemical composition of the phases, the particular phases present, as well as their volume fractions.

Samples containing 50 mass% V_2O_5 and 50 mass% Fe_2O_3 were reacted at 1400°C under a gas mixture of $\text{CO}/\text{CO}_2=3$ for increasing periods of time. The samples were contained in Pt-Rh wire cones as described in paragraph 3.2.4. The EPMA analyses are shown in Table 3.1. For the sample reacted at 2.67 hours a M_3O_4 phase and liquid were identified. In the 8, 16 and 24 hour samples the only phase present was the M_3O_4 phase, as is seen from the XRD patterns in Fig. 3.10. The liquid phase present in the 2.67 hour sample is not indicated on the XRD patterns since the liquid is not crystalline. The variations in chemical composition with reaction time for the $\text{VO}_x\text{-FeO}_y$ oxide phases are shown in Fig. 3.8. and Fig. 3.9. The above data, in combination, indicates reaction times of eight hours to be sufficient to reach equilibrium.

As a check on the homogeneity of the samples and the reliability of the chemical analyses, point counts were made on photomicrographs taken of the samples under reflected light. The samples used were the 10 mass% Fe_2O_3 -90 mass% V_2O_5 (initial composition) sample and the 30 mass% TiO_2 -70 mass% V_2O_5 (initial composition) sample, reacted for 24 hours at 1400°C. From the point counts the volume fractions of the phases present in the sample were calculated. The average sample composition calculated from the volume fraction of phases and the phase analyses was then compared to the composition of the sample mixture with

which the experiment was started. The results are summarised in Table 3.2. It is seen that the average volume fractions of the respective phases in the 10F14* sample are 0.808 ± 0.03 M_2O_3 -phase and 0.192 ± 0.03 M_3O_4 -phase. The 10F14 sample initially contained 0.151 mol V per 1.190 mol Fe, and the calculated mean sample composition corresponds to this initial composition with 0.142 mol V per 1.198 mol Fe. For the 30T14 sample the average volume fractions of the phases are 0.667 ± 0.038 M_3O_5 -phase and 0.333 ± 0.038 M_2O_3 -phase with the initial sample composition 0.428 mol Ti per 0.878 mol V and the calculated composition 0.375 mol Ti per 0.939 mol V. For the Fe_2O_3 - V_2O_5 samples the correlation between the initial and calculated sample compositions is excellent within two decimal places for the composition expressed in mol. For the TiO_2 - V_2O_5 samples the initial and calculated sample compositions correlate only within one decimal place when composition is expressed in mol. However, the correlation between the initial and calculated sample compositions does indicate that the chemical analyses are reliable.

Table 3.2 Volume fractions for 10F14 and 30T14 Samples

Sample	Phase	Initial Composition (mol)	Calculated Composition (mol)	Volume Fraction
10F14	M_2O_3	0.151	0.142	0.808 ± 0.03
	M_3O_4	1.190	1.198	0.192 ± 0.03
30T14	M_3O_5	0.428	0.375	0.667 ± 0.038
	M_2O_3	0.878	0.939	0.333 ± 0.038

*Code clarification: The first two numbers and the following letter together indicate the initial sample composition, the next two code digits indicate the temperature at which the sample was reacted. If more digits follow they indicate the reaction time in minutes. If no digits follow to indicate the reaction time the reaction time was 24 hours. Therefore the 30T14 code means that the sample with the initial composition of 30 mass% TiO_2 -70 mass% V_2O_5 (the 70 mass% V_2O_5 is implied because only TiO_2 - V_2O_5 and Fe_2O_3 - V_2O_5 mixtures were reacted); was reacted at 1400°C for 24 hours. F indicates Fe_2O_3 in the Fe_2O_3 - V_2O_5 samples.

Each mole removed of a V^{5+} by 10 mol, that is 1.12 grams per 1 mol

Table 3.2 Volume fractions for 10F14 and 30T14 Samples

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Table 3.2 Volume fractions for 10F14 and 30T14 Samples

Table 3.1: EPMA Analyses: 50 mass% Fe_2O_3 - 50 mass% V_2O_5 Samples used in Equilibrium Time Determination Experiments at 1400°C

Time Reacted (h) →	2.67		2.67		8		16		24	
Phase Identified →	M_3O_4		Liquid		M_3O_4		M_3O_4		M_3O_4	
Analyses, mol → Analysis No. ↓	Fe	V	Fe	V	Fe	V	Fe	V	Fe	V
1	0.66	0.70	1.20	0.19	0.72	0.65	0.71	0.65	0.69	0.67
2	0.72	0.65	1.20	0.18	0.71	0.65	0.63	0.73	0.69	0.67
3	0.78	0.59	1.18	0.20	0.71	0.66	0.68	0.68	0.68	0.69
4	0.78	0.59			0.68	0.68	0.66	0.70		
5	0.77	0.59			0.71	0.66				
6	0.69	0.67			0.64	0.72				
7					0.69	0.67				
Average mol Fe; mol V →	0.73	0.63	1.19	0.19	0.69	0.67	0.67	0.69	0.69	0.68
Standard Deviation on mol Fe; mol V →	0.05	0.05	0.01	0.01	0.03	0.03	0.03	0.03	0.01	0.01
95% Confidence Limit on mol Fe; mol V →	0.04	0.04	0.01	0.01	0.02	0.02	0.03	0.03	0.01	0.01

Table 3.2: Volume% Phases for 10F14 and 30T14 Samples

Sample →	10F14*		30T14#	
Phase in Sample	M_2O_3	M_3O_4	M_3O_5	M_2O_3
Average Volume Fraction of Phase	0.808	0.192	0.667	0.333
Standard Deviation	0.167	0.167	0.231	0.231
95% Confidence Limit	0.03	0.03	0.04	0.04
Number of fields ^o analysed	13		13	
	mol Fe	mol V	mol Ti	mol V
Initial Sample Composition →	0.151	1.190	0.428	0.878
Calculated Sample Composition →	0.142* ±0.008	1.198 ±0.03	0.375 ±0.011	0.939 ±0.029

*10F14 = 10 mass% Fe_2O_3 -90 mass% V_2O_5 initial composition, reacted at 1400°C

#30T14 = 30 mass% TiO_2 -70 mass% V_2O_5 initial composition, reacted at 1400°C

^oEach field consisted of a 13 by 10 grid, that is 130 points per field

*Calculated sample composition:

$$(X_{vol})_{M_2O_3} = \text{Volume fraction of phase } M_2O_3$$

$$(V_{mol})_{M_2O_3} = \text{Molar volume of phase } M_2O_3$$

$$V_{Total} = \text{Total sample volume}$$

$$X_{M_2O_3} = \text{Mole fraction of phase } M_2O_3$$

$$(molV)_{M_2O_3} = \text{mol V in } M_2O_3 \text{ phase}$$

$$mm_{M_2O_3} = \text{Molar mass of } M_2O_3$$

$$X_{M_2O_3} = \frac{\left(\frac{(X_{vol})_{M_2O_3} \cdot V_{Total}}{(V_{mol})_{M_2O_3}} \right)}{\left(\frac{(X_{vol})_{M_2O_3} \cdot V_{Total}}{(V_{mol})_{M_2O_3}} + \frac{(X_{vol})_{M_3O_4} \cdot V_{Total}}{(V_{mol})_{M_3O_4}} \right)}$$

$$= \frac{(X_{vol})_{M_2O_3} \cdot (V_{mol})_{M_2O_3} \cdot (V_{mol})_{M_3O_4}}{(V_{mol})_{M_2O_3} \cdot (V_{mol})_{M_3O_4} \cdot (X_{vol})_{M_2O_3} + (V_{mol})_{M_2O_3}^2 \cdot (X_{vol})_{M_3O_4}}$$

Similarly, $X_{M_3O_4}$ is calculated.

The average sample composition is calculated as follows:

$$(molV)_{sample} = (molV)_{M_2O_3} \cdot X_{M_2O_3} + (molV)_{M_3O_4} \cdot X_{M_3O_4}$$

$(V_{mol})_{M_2O_3}$ is calculated from the density of V_2O_3 as follows:

$$\rho_{V_2O_3} = 4.870 \text{ g/cm}^3$$

The M_2O_3 phase was analysed to consist of 1.248 mol V and 0.090 mol Fe. This equates to 1.866 mol V and 0.135 mol Fe for 3 mol O, that is $X_V = 0.933$ and $X_{Fe} = 0.067$. There is 0.065 mol V in 4.870 g V_2O_3 . Therefore:

$$(molV)_{new} = (0.933)(0.065) = 0.061 \text{ mol} = 3.087 \text{ g}$$

$$(molFe)_{new} = (0.0673)(0.065) = 0.004 \text{ mol} = 0.246 \text{ g}$$

$$\Rightarrow (g/cm^3)_{new} = 3.330 + (4.870 - 3.311) = 4.889 \text{ g/cm}^3$$

$$mm_{M_2O_3} = 150.57 \text{ g/mol}$$

$$\Rightarrow (V_{mol})_{M_2O_3} = 150.57 / 4.889 = 30.80 \text{ cm}^3 / \text{mol}; \text{ Similarly } (V_{mol})_{M_3O_4} = 45.45 \text{ cm}^3 / \text{mol}$$

$$\rho_{V_3O_4} = 4.762 \text{ g/cm}^3; \rho_{V_3O_5} = 4.724 \text{ g/cm}^3$$

The V_3O_5 density used to calculate the M_3O_5 phase density was adjusted with respect to volume because of a small shift in the X-ray diffraction analyses pattern with respect to the X-ray diffraction reference data for V_3O_5 .

Fig. 3.8: Equilibrium Time Determination - M_3O_4 Phase

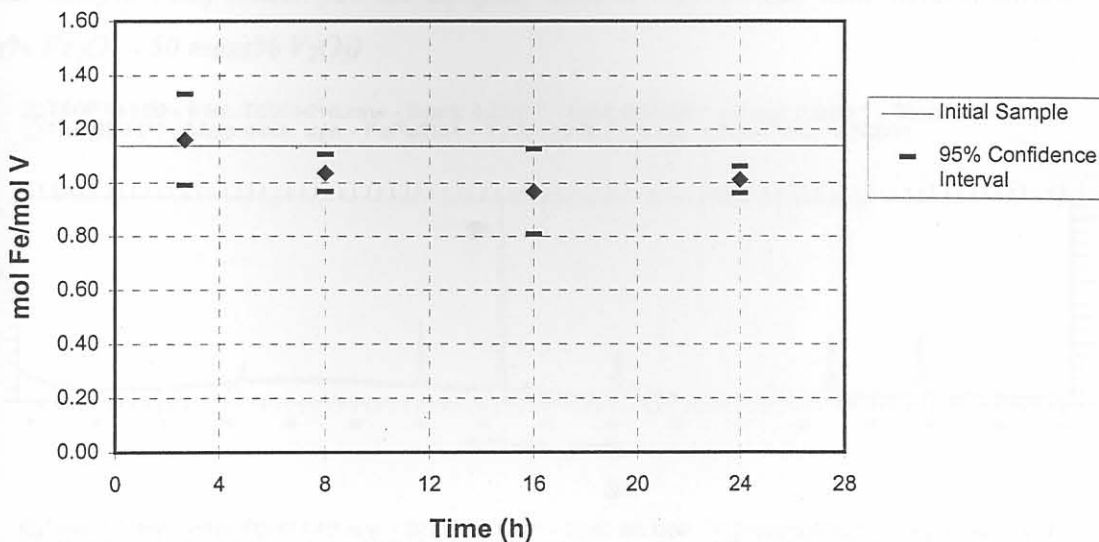
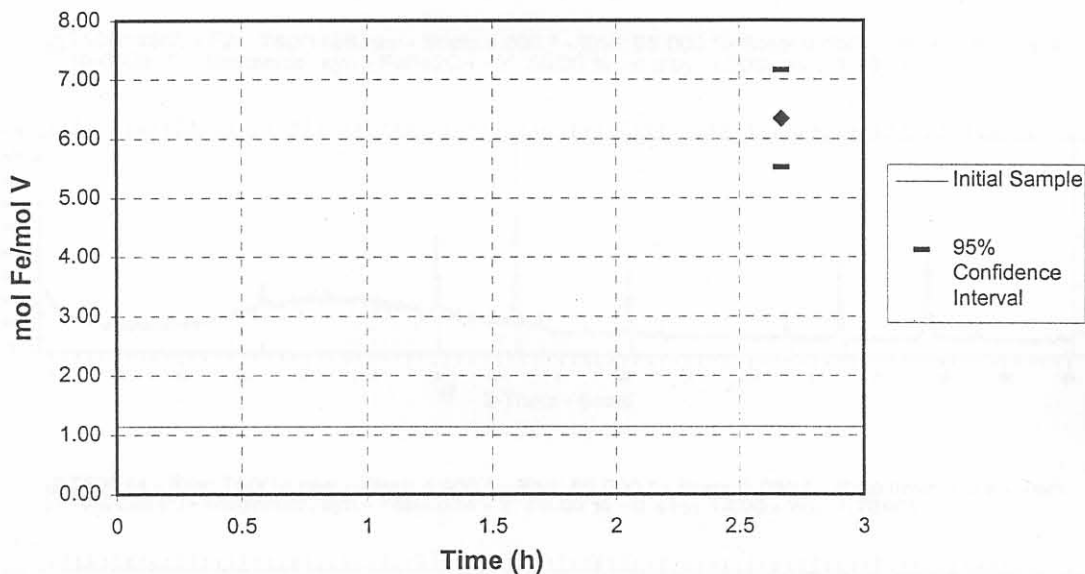


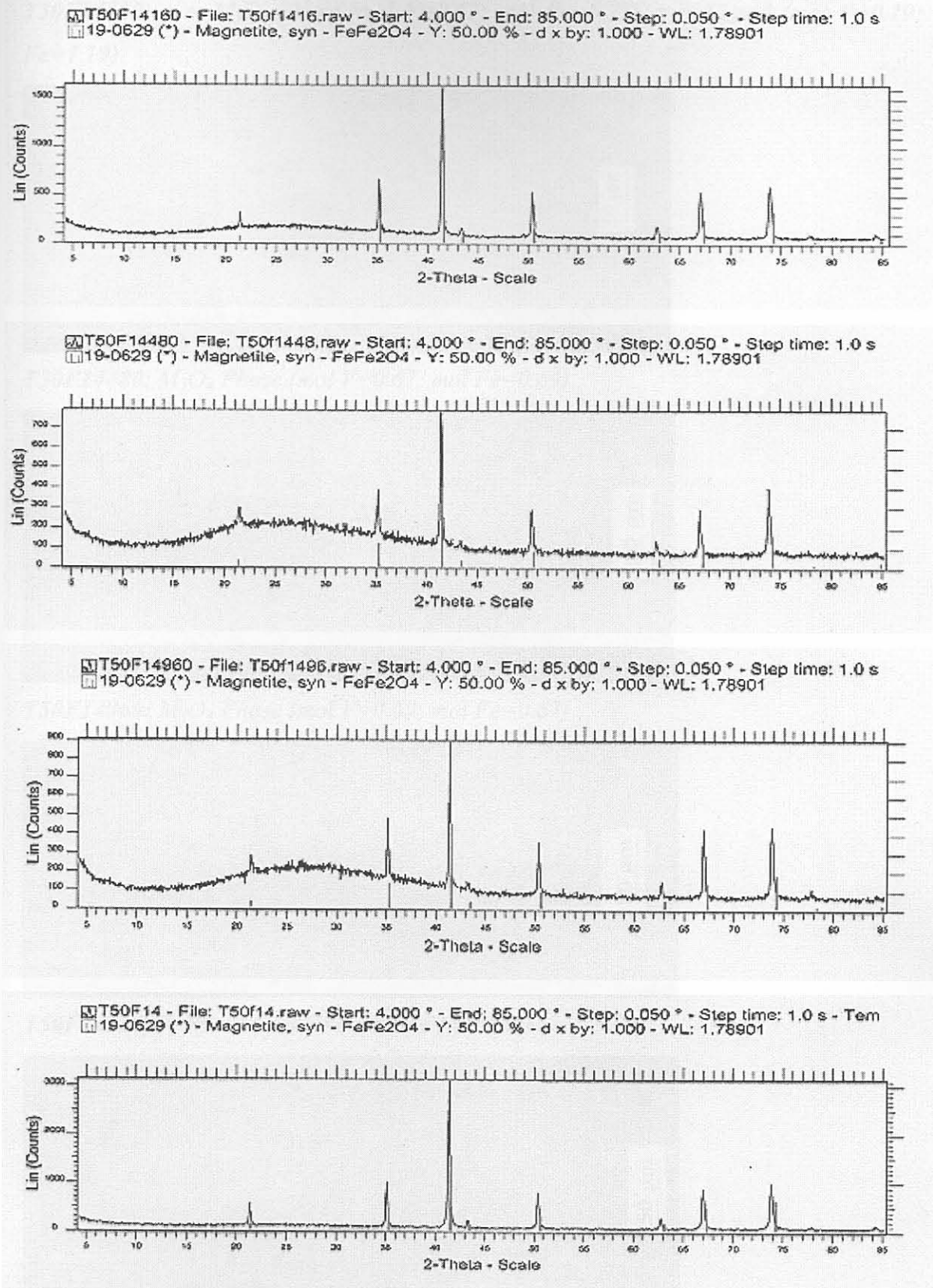
Fig. 3.9: Equilibrium Time Determination - Liquid Phase



T50F14160 = 2.67 hours, T50F14180 = 8 hours, T50F14190 = 16 hours, T50F14 = 24 hours

Fig. 3.10: XRD Patterns for Samples used in Equilibrium Time Determination

(Initial sample composition for all samples used in equilibrium time determination = 50 mass% Fe_2O_3 - 50 mass% V_2O_5)

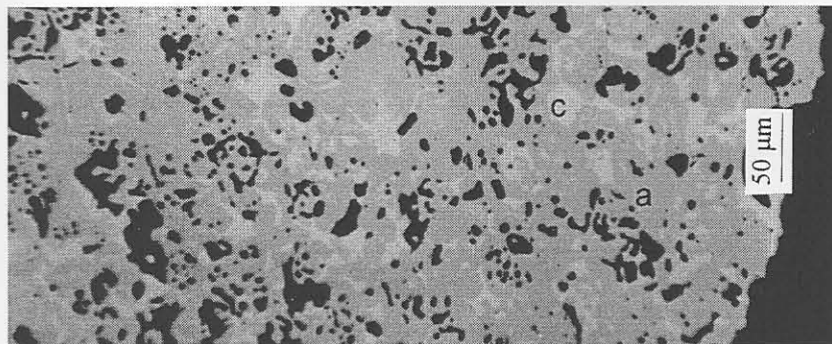


T50F14160 = 2.67 hours; T50F14480 = 8 hours; T50F14960 = 16 hours; T50F14 = 24 hours

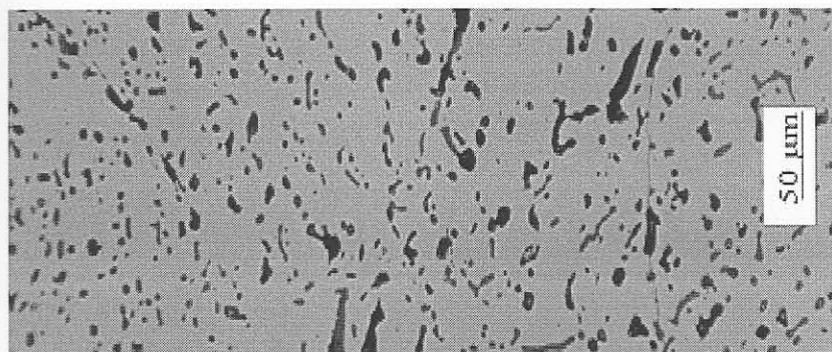
Fig. 3.11: Photomicrographs for Samples used in Equilibrium Time Determination

(Initial sample composition for all samples used in equilibrium time determination = 50 mass% Fe_2O_3 - 50 mass% V_2O_5)

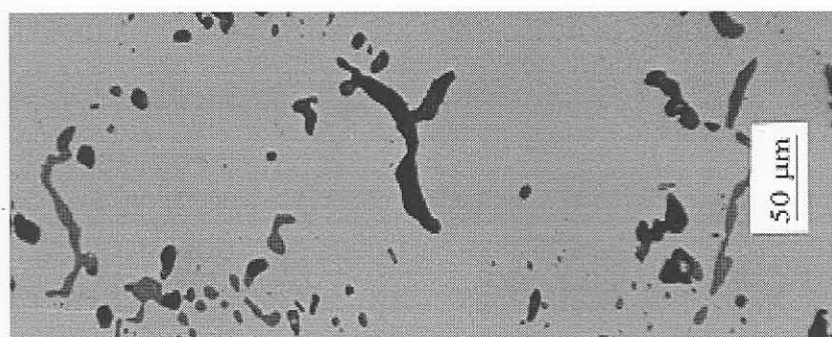
T50F14160: a = M_3O_4 Phase (mol V=0.63; mol Fe=0.73), c = Liquid (mol V=0.19; mol Fe=1.19)



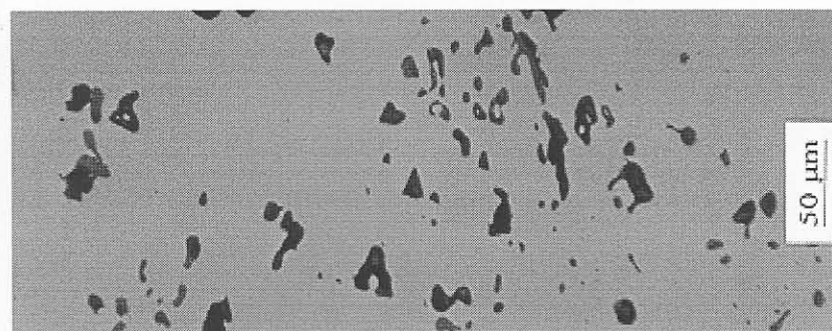
T50F14480: M_3O_4 Phase (mol V=0.67; mol Fe=0.69)



T50F14960: M_3O_4 Phase (mol V=0.69; mol Fe=0.67)



T50F14: M_3O_4 Phase (mol V=0.68; mol Fe=0.69)



T50F14160 = 2.67 hours; T50F14480 = 8 hours; T50F14960 = 16 hours; T50F14 = 24 hours

3.4. Conclusion

The experimental apparatus and procedure described is suitable for studying phase relations in Fe_2O_3 - V_2O_5 mixtures under partial oxygen pressures fixed by a CO/CO_2 gas mixture, with a reaction time of at least eight hours at $1400^\circ C$.

The sample holders facilitate good contact between the sample and the gas mixture so that the required reaction time for the attainment of chemical equilibrium is short. Employing the quench technique allows quenching of the reacted sample without reoxidation which would have occurred if the sample came into contact with oxygen in the air at experimental temperatures.

Sample No.	wt% Fe_2O_3	wt% V_2O_5	Reaction Time (h)	Phase(s)	Crystal Structure
1	100	0	24	Fe_2O_3	$R\bar{3}m$
2	90	10	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
3	80	20	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
4	70	30	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
5	60	40	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
6	50	50	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
7	40	60	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
8	30	70	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
9	20	80	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
10	10	90	24	Fe_2O_3 , M_2O_3	$R\bar{3}m$, $Trigonal$
11	0	100	24	V_2O_5	$C2/m$

The phase diagram Fe_2O_3 - V_2O_5 phase diagram constructed from the experimental data is shown in Fig. 4.3, and a summary of the EPMA analyses is given in Appendix 3 and Appendix 4. The phase fields identified are Fe_2O_3 , M_2O_3 , $Fe_2O_3 + M_2O_3$ and Magnet phases, with M designating both vanadium and titanium ions existing within the particular crystal structure. As mentioned earlier, Magnet phases are crystallographic phase structures represented by the general formula T_2O_{3+2n} for T-O mixtures.²² The phases with $4 \leq n \leq 10$ have crystal structures derived from the spinel structure.¹² Phases with $n > 10$ have structures based on other their parent and on some different families of phases.²³ Both vanadium and titanium oxides form Magnet phases.²⁴⁻²⁶

The XRD patterns for the series of samples reacted at $1400^\circ C$ are shown in Fig. 4.4. The corresponding photomicrographs for the samples are shown in Fig. 4.5. In Table 4.2 the