MICROSTRUCTURE AND RESPONSE STUDIES OF CHROMIUM TITANIUM OXIDE GAS-SENSITIVE RESISTORS

KHALID SHUKRI

PhD

UNIVERSITY COLLEGE LONDON

FEBRUARY 1999
This thesis is dedicated to the memory of my father
ABSTRACT

The aim of this project was to investigate the effects of microstructure and composition on the response of gas sensitive resistors fabricated from chromium titanium oxide powders.

The methods of preparation were varied in order to vary the microstructure in the resulting devices. The chromium oxide starting material was obtained both by decomposition of ammonium dichromate, and by colloidal precipitation. Titanium dioxide was obtained by colloidal precipitation. Mixing both with and without the addition of surfactants was explored. Several compositions were prepared in each method and sintered at various firing temperatures. Changing the composition by varying the titanium content had a small effect on the response, which increased slightly as the titanium content was increased. Changing the microstructure by altering the preparation method or increasing the sintering time had a more prominent effect on the response, the response decreasing as the structure became more agglomerated and increasing to some of the test gases when the small grains were grown through prolonged sintering times. Agglomeration and grain-growth in the printed layers dominated the behaviour of the devices prepared from the powders.

It was discovered that certain bonding agents used in printing the gold electrodes migrated into the oxide layer during the process of firing the oxide onto the substrate. The concentration of these fluxes was dependent on the preparation temperature of the sensors, and as this increased both the response of the sensor and its variation with depth within the porous oxide layer were affected.
TABLE OF CONTENTS

Title page 1
Abstract 3
Table of contents 4
Table of figures 9
Table of tables 17
Table of abbreviations 18
Acknowledgements 19

CHAPTER 1. INTRODUCTION 20

1.1 General 21
    1.1.1 Organisation Of Thesis 25
1.2 Simplified Electronic Band Theory Applied 27
    To Semiconducting Oxides
1.3 Gas Response Model 30
1.4 Reaction – Diffusion Effects In Ceramic 35
    Oxide Gas – Sensitive Resistors
1.5 Microstructure 38
    1.5.1 Polycrystalline Materials 38
    1.5.2 Control Of Microstructure 39
1.6 Colloidal Systems 42
1.7 Phase Relations Of The Cr₂O₃-TiO₂ System 43
CHAPTER 2. EXPERIMENTAL

2.1 General

2.2 Equipment Used

2.3 Powder Preparation

   2.3.1 Method One

   2.3.2 Method Two

   2.3.3 Method Three

   2.3.4 Method Four

   2.3.5 Standard Preparation For Epma

2.4 Powder Sintering

2.5 Ink Preparation

2.6 Screen Printing

2.7 Firing Of Sensors

2.8 Gas Rig Experiments

2.9 Analytical Techniques

   2.9.1 General

   2.9.2 Scanning Electron Microscopy

   2.9.3 Energy Dispersive Analysis Of X-Rays

   2.9.4 Electron Probe Microanalyser

   2.9.5 X-Ray Powder Diffraction (XRD)

   2.9.6 X-Ray Photoelectron Spectroscopy

2.10 Experimental Error

2.11 Variability Experiments

   2.11.1 General

   2.11.2 Gas Rig Experiments

   2.11.3 Base Line Resistance Shift
CHAPTER 3. PHYSICOCHEMICAL PROPERTIES OF CHROMIUM TITANIUM OXIDE

3.1 Method One
   3.1.1 General
   3.1.2 Sample Preparation
   3.1.3 Electron Microprobe Studies
   3.1.4 Bulk Vs. Surface Composition
   3.1.5 X-Ray Diffraction Studies
   3.1.6 Scanning Electron Microscopy Studies

3.2 Method Two
   3.2.1 General
   3.2.2 Sample Preparation
      3.2.2.1.1 Electron Microprobe Studies
      3.2.2.1.2 X-Ray Photoelectron Spectroscopy
      3.2.2.1.3 Bulk Vs. Surface Composition
      3.2.2.1.4 X-Ray Diffraction Studies
      3.2.2.1.5 Scanning Electron Microscopy Studies
   3.2.2.2 Effect Of Sintering Time
      3.2.2.2.1 X-Ray Photoelectron Studies
      3.2.2.2.2 X-Ray Diffraction Studies
      3.2.2.2.3 Scanning Electron Microscopy Studies

3.3 Method Three
   3.3.1 General
   3.3.2 Sample Preparation
   3.3.3 Electron Microprobe Studies
   3.3.4 X-Ray Photoelectron Spectroscopy Studies
   3.3.5 Bulk Vs. Surface Composition
3.3.6 X-Ray Diffraction Studies 112
3.3.7 Scanning Electron Microscopy Studies 115

3.4 Comparison Between Methods 117
  3.4.1 General 117
  3.4.2 X-Ray Photoelectron Studies 117
  3.4.3 X-Ray Diffraction Studies 120
  3.4.4 Scanning Electron Microscopy Studies 122

3.5 Effect Of Substrate Firing Temperature On Response 123
  3.5.1 General 123
  3.5.2 Gas Rig Results 124
  3.5.3 Concentration Gradient Results 129
  3.5.4 Electron Microprobe Studies 132

3.6 Surface Catalysed Combustion 138
  3.6.1 General 138
  3.6.2 Theory 139
  3.6.3 Experimental 140
    3.6.3.1 Apparatus 140
    3.6.3.2 Experiment Design 140
    3.6.3.3 Detector Calibration 140
  3.6.4 Results And Discussion 143
    3.6.4.1 Switched Gas Experiment 143
      3.6.4.1.1 Carbon Monoxide Combustion 143
      3.6.4.1.2 Acetone Combustion 145
      3.6.4.1.3 Ammonia Combustion 147
    3.6.4.2 Constant Gas Experiment 148
      3.6.4.2.1 Carbon Monoxide Combustion 148
      3.6.4.2.2 Acetone Combustion 151
      3.6.4.2.3 Ethanol Combustion 154
    3.6.4.3 Temperature Programmed Desorption Experiment 157
CHAPTER 4. GAS RESPONSE OF CHROMIUM TITANIUM OXIDE

4.1 General
4.2 Method One
4.3 Method Two
   4.3.1 Response Variation With Sensor Composition & Sintering Temperature
   4.3.2 Response Variation With Powder Sintering Time And Temperature
4.4 Method Three
4.5 Method Four
   4.5.1 Effect Of Pellet Sintering On Response
   4.5.2 Effect Of Sintering Time & Temperature On Baseline Resistance
4.6 Response Comparison Between Methods 1, 2 & 3
4.7 Effect Of Alumina Addition To Chromium Titanium Oxide
   4.7.1 General
   4.7.2 Gas Rig Results

CHAPTER 5. DISCUSSION OF RESULTS

5.1 Summary
5.2 Discussion
5.3 Conclusion

REFERENCES

Appendices A & B
# TABLE OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Energy band characterising a semiconductor</td>
<td>28</td>
</tr>
<tr>
<td>1.2</td>
<td>Energy band diagram</td>
<td>29</td>
</tr>
<tr>
<td>1.3</td>
<td>Charge exchange on the surface of a grain</td>
<td>30</td>
</tr>
<tr>
<td>1.4</td>
<td>Schematic representation of a grain structure in a porous solid</td>
<td>31</td>
</tr>
<tr>
<td>1.5</td>
<td>Schematic showing thin film gas sensor</td>
<td>32</td>
</tr>
<tr>
<td>1.6</td>
<td>A model set by Yamauchi that accounts for grain size effects</td>
<td>34</td>
</tr>
<tr>
<td>1.7</td>
<td>Experimental responses R/R₀ of large and small electrodes</td>
<td>36</td>
</tr>
<tr>
<td>1.8</td>
<td>Diagram representing self-diagnostic device with two pairs of electrodes</td>
<td>37</td>
</tr>
<tr>
<td>1.9</td>
<td>Self-diagnostic sensor with three gaps</td>
<td>37</td>
</tr>
<tr>
<td>1.10</td>
<td>Progressive stages of sintering</td>
<td>40</td>
</tr>
<tr>
<td>1.11</td>
<td>The dihedral angle and its effect on the amount of grain-to-grain contact</td>
<td>41</td>
</tr>
<tr>
<td>1.12</td>
<td>a) Unit cell of rutile b) Interrelation of basic rutile-type structure of adjacent slabs of Ti₅O₉</td>
<td>44</td>
</tr>
<tr>
<td>2.1</td>
<td>Regression of chromium and titanium standards as a function of the target composition</td>
<td>51</td>
</tr>
<tr>
<td>2.2</td>
<td>All glass apparatus for the study of gas response of multiple self-heated sensor elements</td>
<td>55</td>
</tr>
<tr>
<td>2.3</td>
<td>Wheatstone bridge arrangement used in rig setup</td>
<td>56</td>
</tr>
<tr>
<td>2.4</td>
<td>Typical gas response trace for powder prepared by method one</td>
<td>57</td>
</tr>
<tr>
<td>2.5</td>
<td>Diagram showing backscattered and secondary electron emission and the detector</td>
<td>60</td>
</tr>
</tbody>
</table>
2.6 Typical EPMA map of a sectioned gas sensor 63
2.7 SEM micrograph of a sectioned gas sensor 64
2.8 Bragg’s law for X-ray diffraction 65
2.9 X-ray powder diffraction data for Cr₂O₃ (Aldrich), Ti/(Ti+Cr) = 10.63 and 5.34 %, prepared by method four 68
2.10 A one electron energy level diagram 69
2.11 Typical example of an XPS spectrum for powder prepared by method one 71
2.12 Response of five identical devices prepared using method one 74
2.13 Concentration gradient of five identical devices prepared using method one 75
2.14 Base line resistance variation for all devices tested, (method one) 76

3.1 XPS data showing amount of chromium, titanium, oxygen and Ti/(Ti+Cr)% on the surface as a function of composition for powders prepared using method one 81
3.2 Surface / bulk comparison for titanium and chromium across the series for preparation method one 82
3.3 XRD pattern for all four samples prepared using method one 84
3.4 SEM micrographs samples prepared using method one 87
3.5 XPS surface analysis data for titanium, chromium, oxygen and Ti/(Ti+Cr) ratio for samples prepared by method two 92
3.6 Surface bulk comparison for various composition sintered at 1000 °C for one hour prepared by method two 95
3.7 XRD pattern of (Ti30) powder, (method two) 96
3.8 Cr₂O₃ peak shift as a function of sintering temperature for powders prepared by method two 97
3.9 Crystallite size of oxide powders prepared using method two
3.10 SEM micrographs of Ti/(Ti+Cr) = 0.33 and 1.15%, prepared using method two
3.11 SEM micrographs of Ti/(Ti+Cr) = 4.42 and 6.40%, prepared using method two
3.12 XPS surface analysis data for chromium, titanium, oxygen and Ti/(Ti+Cr) ratio for powders prepared by method two and sintered at 15 min., 1, 4 and 12 hours at 1000 °C
3.13 X-ray diffraction pattern of powders prepared by method two and sintered for 15 minutes, 1, 4, 12 hrs at 1000 °C and 12 hrs at 1200 °C
3.14 Crystallite size variation given sintering time at constant temperature of 1000 °C for powders prepared by method two (target composition Cr$_{1.8}$Ti$_{0.2}$O$_3$)
3.15 SEM micrographs of samples sintered for 15 minuets, 1, 4 and 12 hrs at 1000 °C & 12 hrs at 1200 °C, prepared by method two (target composition Cr$_{1.8}$Ti$_{0.2}$O$_3$)
3.16 XPS data showing chromium, titanium, oxygen and Ti/(Ti+Cr) concentration on the surface as a function of composition for samples prepared by method three
3.17 Surface and bulk concentration for chromium, titanium and Ti/(Ti+Cr) as a function of composition for samples prepared by method three
3.18 X-ray diffraction pattern of powders prepared by method three
3.19 Peak position of Cr$_2$O$_3$ for all powders prepared by method three as a function of actual composition
3.20 SEM micrographs of powders prepared by method three
3.21 XPS data showing titanium, chromium, oxygen
and Ti/(Ti+Cr)% ratio on the surface for powders prepared by methods one, two and three

3.22 Crystallite size of powders prepared by methods one, two and three as a function of composition

3.23 $\text{Cr}_2\text{O}_3$ peak position of powders prepared by methods one, two and three as a function of composition

3.24 Response of sensors whose substrates were fired at 750, 800, 850 and 900 °C to different test gases at 350 °C operating temperature, (method one, theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$)

3.25 Response of sensors whose substrates were fired at 750, 800, 850 and 900 °C to different test gases at 400 °C operating temperature, (method one, theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$)

3.26 Concentration gradient for devices fired at 750, 800, 850 and 900 °C and operated at 350 °C, (method one, theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$)

3.27 Concentration gradient for devices fired at 750, 800, 850 and 900 °C and operated at 400 °C, (method one, theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$)

3.28 Electron microprobe data showing two sectioned sensors fired at 700 and 900 °C for a) cadmium, b) copper and c) calcium elements, (method one, theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$)

3.29 Electron microprobe data showing two sectioned sensors fired at 700 and 900 °C for a) magnesium, b) iron and c) silicon elements, (method one, theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$)

3.30 Electron microprobe data showing two sectioned sensors fired at 700 and 900 °C for a) chromium and b) titanium elements, (method one, theoretical
composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$)

3.31 Electron microprobe data showing two sectioned sensors fired at 700 and 900 °C for a) aluminium and b) gold elements, (method one, theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$)

3.32 Surface catalysed combustion experiment

3.33 Calibration curve for carbon monoxide, acetone, ethanol and ammonia

3.34 Switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with carbon monoxide as test gas

3.35 Rate constant for switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with carbon monoxide as a test gas

3.36 Switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with acetone as test gas

3.37 Rate constant for switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with acetone as a test gas

3.38 Switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with ammonia as test gas

3.39 Constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with carbon monoxide as test gas

3.40 Constant gas experiment for powder prepared by method four and sintered at 1200 °C for 12 hour with carbon monoxide as test gas

3.41 Rate constant for constant gas experiment for powder prepared by method four and sintered at 1000 °C
for 1 hour and 1200 °C for 12 hours with carbon monoxide as a test gas

3.42 Constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with acetone as test gas

3.43 Constant gas experiment for powder prepared by method four and sintered at 1200 °C for 12 hour with acetone as test gas

3.44 Rate constant for constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour and 1200 °C for 12 hours with acetone as a test gas

3.45 Constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with ethanol as test gas

3.46 Constant gas experiment for powder prepared by method four and sintered at 1200 °C for 12 hour with ethanol as test gas

3.47 Rate constant for constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour and 1200 °C for 12 hours with ethanol as a test gas

3.48 Combustion experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with ammonia as a test gas

3.49 Combustion experiment for powder prepared by method four and sintered at 1200 °C for 12 hours with ammonia as a test gas

4.1 Raw data for typical experiment, resistance as a function of time and [CO], for sensors prepared by method one

4.2 Typical response law fit, resistance as a
4.3 Values of $\beta$ for all sensors prepared using method one as a function of composition

4.4 Response of all sensors prepared using method one as a function of composition

4.5 Response gradient of sensors prepared using method one as a function of composition

4.6 Raw data for typical experiment, resistance as a function of time, for sensors prepared by method two

4.7 Raw data for typical experiment, resistance as a function of gas concentration, for sensors prepared by method two

4.8 Values of $\beta$ for all sensors prepared using method two as a function of composition

4.9 Response of all sensors prepared by method two and sintered at 800, 900 and 1000 $^\circ$C

4.10 Concentration gradient of all sensors prepared by method two and sintered at 800, 900 and 1000 $^\circ$C as a function of composition

4.11 Response for powders prepared by method two and sintered at 1000 and 1200 $^\circ$C

4.12 Values of $\beta$ for all sensors prepared using method three as a function of composition

4.13 Response of all sensors prepared by method three as a function of composition

4.14 Concentration gradient of all sensors prepared by method three as a function of composition

4.15 Response to CO, wet CO and relative humidity for all powders prepared by method four at 350 $^\circ$C operating temperature

4.16 Response to CO, wet CO and relative humidity for all powders prepared by method four at 400 $^\circ$C
operating temperature

4.17 Response for various devices prepared by method four and operated at 400 °C

4.18 Response for various devices prepared by method four and operated at 350 °C

4.19 Effect of baseline resistance on devices prepared by method four and operated at 400 °C.

4.20 Effect of baseline resistance on devices prepared by method four and operated at 350 °C

4.21 Response as a function of composition for some of the sensors prepared by methods 1, 2 and 3

4.22 X-ray diffraction pattern of \([\text{Cr}_{1.8-x}\text{Ti}_{0.2}(\text{Al}_2\text{O}_3)_x\text{O}_3] \), where \(x = 0.1 \) to 0.3

4.23 Response to \([\text{Cr}_{1.8-x}\text{Ti}_{0.2}(\text{Al}_2\text{O}_3)_x\text{O}_3] \), where \(x = 0.1 \) to 0.3] for four test gases operated at 350 °C

4.24 Concentration gradient to \([\text{Cr}_{1.8-x}\text{Ti}_{0.2}(\text{Al}_2\text{O}_3)_x\text{O}_3] \), where \(x = 0.1 \) to 0.3] for four test gases operated at 350 °C

5.1 Gas response law

Appendix A Highly magnified cross-section area of a sensor looking from the base of the electrodes (small gap) to the top of the oxide layer (sample prepared using method one, \(\text{Ti}/(\text{Ti}+\text{Cr}) = 5.34\%\), substrate fired at 700 °C)

Appendix B Highly magnified cross-section area of a sensor looking from the base of the electrodes (small gap) to the top of the oxide layer (sample prepared using method one, \(\text{Ti}/(\text{Ti}+\text{Cr}) = 5.34\%\), substrate fired at 900 °C)
# TABLE OF TABLES

<table>
<thead>
<tr>
<th>Table of contents</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table of figures</td>
<td>9</td>
</tr>
<tr>
<td>Table of tables</td>
<td>17</td>
</tr>
<tr>
<td>Table of abbreviations</td>
<td>18</td>
</tr>
<tr>
<td>1.1 Classification of sensor material</td>
<td>33</td>
</tr>
<tr>
<td>2.1 Analytical techniques used and their benefits</td>
<td>46</td>
</tr>
<tr>
<td>2.2 Target and EPMA analysed composition of standard</td>
<td>50</td>
</tr>
<tr>
<td>3.1 Measured stoichiometry of powders prepared using method one</td>
<td>80</td>
</tr>
<tr>
<td>3.2 XRD data showing crystallite size and peak position of samples prepared using method one</td>
<td>85</td>
</tr>
<tr>
<td>3.3 Measured stoichiometry of powders prepared using method two (sintered at 1000 °C for one hour)</td>
<td>90</td>
</tr>
<tr>
<td>3.4 Peak position variation of Cr₂O₃ for different sintering times at constant 1000 °C for samples prepared by method two</td>
<td>104</td>
</tr>
<tr>
<td>3.5 Electron microprobe data for method three, showing measured composition ratio of oxide powders</td>
<td>108</td>
</tr>
<tr>
<td>3.6 Crystallite size variation for samples prepared by method three as a function of actual composition</td>
<td>112</td>
</tr>
</tbody>
</table>
# TABLE OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CTO</td>
<td>Chromium titanium oxide</td>
</tr>
<tr>
<td>EDAX</td>
<td>Energy dispersive analysis of X-rays</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron probe micro analyser</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I would like to thank Professor David Williams for his supervision throughout my work. My thanks also go to Dr Keith Pratt for his constant advice and practical help.

My thanks goes to Capteur Sensors and Analysers Ltd. for funding.

My thanks to the technical staff at UCL especially David Knapp and also Kevin Reeves at the institute of Archaeology who carried out the EPMA analysis and helped considerably in the SEM imaging.

I would also like to thank all the people at lab G15 especially Luba, George, Vincent, Stef, Julian, Paul and Dirk.

My sincere thanks to both my mother and my sister for their moral support.
CHAPTER ONE

INTRODUCTION
CHAPTER ONE

INTRODUCTION

1.1 GENERAL

Gas sensors are playing a crucial part in the industrialised society we live in today, where they are used constantly in monitoring and controlling air pollution in the environment and in various domestic and technical installations around the world.¹

Sensors should be able to work continuously so that they monitor the concentration of a particular gas and prevent accidents due to leakage, thus saving lives and equipment. As these devices are being used in industry they have to be durable and non-contaminating, and as more sensors are used in the home, they need to be portable (small in size) and inexpensive (simple fabrication).

One example of a major area where gas sensors are playing an important role is in the motor industry. It is known that emissions from the internal combustion engine in motor vehicles are one of the main contributors to atmospheric pollution. The control over the amount of exhaust fumes being emitted to the atmosphere has come a long way, especially since the introduction of the catalytic converter.
The pollution arises because the fuel is incompletely burnt, and so hydrocarbons and carbon monoxide are emitted. Also, oxides of nitrogen are produced due to the high flame temperature in the combustion chamber during ignition where atmospheric nitrogen is oxidised. By using electrical ceramic devices to control the air-fuel ratio of petrol fuelled engines, a huge reduction in the amount of pollutants emitted to the atmosphere has been obtained. This advance has also lead to a more fuel-efficient engine. For this application, a potentiometric device utilising a high-temperature oxygen ion conductor (ZrO\textsubscript{2}/Y\textsubscript{2}O\textsubscript{3}) is preferred, although gas sensitive resistors have also been used. Another example of an important application area is carbon monoxide emission from poorly maintained gas-burning appliances in the home. Gas-sensitive resistors are currently the most widely applied technology in this area.

Gas sensitive resistors are based on a ceramic substrate, which carries a set of electrodes on one side and a heater track on the other. A porous layer of an active oxide is usually deposited on the electrodes. This oxide often carries a catalytic metal such as platinum or palladium and other additives, which are claimed to enhance selectivity to different gases. These devices are robust, inexpensive, small and reliable. They are widely used for industrial and domestic health and safety monitoring. Since their invention in the 1960's, they have been the subject of extensive research, directed both at understanding the mechanism of response and improving the performance, particularly in respect of the characteristic of ageing, drift and long-term stability.
Work in the field of semiconducting oxide gas sensors first started as early as 1962 by Seiyama et al in Japan, where they attempted to use thin films of zinc oxide as a gas chromatographic detector instead of the ordinary thermal conductivity cell. Work by Taguchi in Japan resulted, in 1968, in a patent for a gas sensor using sintered tin dioxide. Taguchi found that the addition of small quantities of palladium or platinum had the effect of improving the sensitivity of metal oxide gas sensors, and that an organic silica binder gave an excellent long term stability to the SnO₂ ceramic-type gas sensor. Ten years later, a γ-Fe₂O₃ ceramic sensor was produced commercially, and some years later again the TiO₂ ceramic-type O₂ sensor was developed.

Work by other groups has shown that semiconducting oxides are exhibiting promise for the detection of H₂S, NH₃, PH₃, Cl₂ and NOₓ. The mechanism of the response to these gases might vary from one gas to the other, since they have rich redox chemistry and can in principle co-ordinate directly to the oxide surface. More recently, titanium substituted chromium oxide sensors have been used as detectors for combustible gases such as hydrocarbons and carbon monoxide.

These gas sensitive resistors respond to the presence of small concentrations (ppm) of impurities in air by alteration of the surface conductivity. They are highly durable and inexpensive. The mechanism for the response is understood to be that the bulk resistance of the porous solid is primarily determined by the coverage of ionosorbed oxygen species acting as electron traps. If the reaction of these species with the gas-phase results in a change in the coverage, then the overall electrical resistance of the solid will change.
There are a number of problems with most of the devices that are based on one pair of electrodes. They generally tend to be sensitive to too many gases, suffer from slow base line drift and are affected by variations in humidity. The oxide can also be poisoned by species such as silicones, which will affect the response of the sensor and go undetected by the operator. One way to overcome some of these problems is to use a self-diagnostic sensor array device.

Another problem with gas-sensitive resistors is lack of manufacturing reproducibility. In part this may stem from subtle effects of microstructure on response. Effects of microstructure on response are to be expected because the measurement is of conductivity, which is nominally a bulk property but which is affected by electron trap states at the interface and also by the properties of the contacts between the crystallites in a porous solid. At least, effects of crystallite size and porosity are to be expected.

The effect of microstructure on response of a particular type of gas-sensitive resistor is the central theme of this thesis. Research on the effects of variation of the microstructure would be to alter concentration gradients of gases within the porous sensing layer. The studies employed devices constructed of an array of electrodes of different spacing to probe variations of response with depth within the fabricated structure.
1.1.1 ORGANISATION OF THESIS

In this thesis the effects of varying the microstructure (preparation methods), grain size (sintering time and temperature) or the composition (titanium content) on the response of the gas sensitive resistors based on \( \text{Cr}_{2-x}\text{Ti}_x\text{O}_3 \) \((0<x<0.4)\) will be described.\textsuperscript{17}

In the introduction, the theories of response will be described and the effects of microstructure considered in terms of electronic properties and reaction diffusion. Ways to control the microstructure will be discussed and a description of some of the synthesis methods used will be given.

In the second chapter, experimental techniques are described. These include all methods of sensor preparation, gas rig experiments and the analytical techniques (SEM, EDAX, EPMA, XRD and XPS). The variability of the sensor response for different devices prepared using a fixed composition and synthesis method is presented, as the basis for estimation of experimental errors.

In the third chapter, the physicochemical properties of chromium titanium oxide will be discussed for all the preparation methods. The interaction between sensor material and substrate is addressed here. The study of the rate of surface catalysed combustion of the test gases over different material preparation is also presented, since it represents essential background for understanding the response behaviour.

The response of the sensors for all the methods and compositions at different operating temperatures will be discussed in chapter four. The effect of aluminium substitution is also considered here.
Chapter five presents the discussion of the results, drawing together the different factors which affect the response and making further comment on source of variability of behaviour.
1.2 SIMPLIFIED ELECTRONIC BAND THEORY APPLIED TO SEMICONDUCTING OXIDES

One of the important properties of a semiconductor for its electrical behaviour is the concentration of charge carriers. As semiconductors in general contain relatively few free charge carriers, this facilitates control of the concentration and behaviour of these charge carriers by external means. In an absolutely clean semiconductor there are equal amounts of negative free electrons and positive free holes, created by the excitation of valence electrons from the valence states in the crystal to the first band of excited states, the conduction band. By such thermal excitation free electrons are formed in the conduction band, leaving unoccupied valence states, which may be considered as free charge carriers also, positively charged, called holes (figure 1.1).

The mass action law controls the concentration of the two carriers and in application to the reaction:

\[ h^+ + e^- \leftrightarrow \text{crystal} \]

gives

\[ np = n_i^2 \quad (1) \]

Where \( n \) and \( p \) are the electron and hole concentrations respectively and \( n_i \) is a constant. In a clean semiconductor \( n \) and \( p \) are equal because it is electrically neutral, therefore both \( n \) and \( p \) are equal to \( n_i \), the intrinsic carrier concentration.

Both \( n \) or \( p \) can be increased by doping. If it is considered that a semiconductor is doped by \( N_D \) donors per unit volume and the donors are assumed to be dissociated completely to positive ions and conduction electrons, then two equations have to be fulfilled, equation (1) and the electrical neutrality condition:
\[ n = p + N_D \]  

Electron energy

\[ n = n_i \exp \left( \frac{q \phi_F}{kT} \right) \]  

(3)

Where \( q \) is the electron charge. Holes are related to the same chemical potential or Fermi energy, thus from eq. (1):

\[ p = n_i \exp \left( -\frac{q \phi_F}{kT} \right) \]  

(4)

Figure 1.1. Energy band characterising a semiconductor

Usually \( N_D \) is much larger than \( n_i \), so \( N_D \) determines \( n \): \( n = N_D \). An n-type semiconductor is formed and dominated by electron conduction. A p-type semiconductor may be formed in the same way by doping with acceptor species, which behave negatively charged by trapping electrons from the valence band.

The electron concentration can also be described in terms of chemical potential or Fermi energy \( \phi_F \)

\[ n = n_i \exp \left( \frac{q \phi_F}{kT} \right) \]  

(3)
In considering the electronic structure of a solid formed from atoms each able to contribute one electron, there will be $N$ atomic orbitals and hence $N$ molecular orbitals squashed into a band. The electrons close to the top of the band can be excited thermally due to the orbitals in the band are so close together. Assuming $T=0$, all the electrons will occupy the lowest available orbitals and only the lowest $1/2N$ molecular orbitals are occupied. The highest occupied molecular orbital in this case is the Fermi level and the smallest amount of energy will excite the uppermost electrons, which will give rise to electrical conductivity, figure (1.2).

![Energy band diagram](image)

**Figure 1.2. Energy band diagram.**
1.3 Gas Response Model

Oxygen abstracts electrons from the bulk of the solid to form surface oxygen ions ($O_2^-$, $O^-$, $O^{2-}$) as it adsorbs at the gas-solid interface. Therefore oxygen can be thought of as a surface trap for electrons from the bulk (figure 1.3). In an n-type semiconductor the electrons come from the donors via the conduction band, therefore the charge carrier concentration at the interface is reduced and an electrical potential barrier to charge transport is developed. The adsorption of further oxygen is hindered as the surface charge is developed; hence the adsorption rate is reduced because the charge must be transferred to the adsorbate over the developing surface barrier.\textsuperscript{14-16,18,22-25}

![Figure 1.3. Charge exchange on the surface of a grain.](image)

The resistance at the junctions between the grains of the solid may be high due to the depletion layer and the potential barrier, and so may dominate the resistance of the solid (figure 1.4). Hence the electrical resistance of the solid may be sensitive to the coverage of the oxygen ions and any factor that changes this will change the resistance of the solid.\textsuperscript{26-28}
For instance, in the presence of a reactive gas, the surface coverage of adsorbed oxygen species might be decreased due to surface catalysed combustion, which will lead to a resistance decrease due to the reduction in the surface potential barrier height and depletion length.

![Figure 1.4. Schematic representation of a grain structure in a porous solid.](image)

The depletion layer thickness $d_{sc}$, which is the depth into the solid that is depleted of conduction electrons as a result of the trapping of electrons in a state localised at the surface, the surface barrier height $\phi_s$, the charge $Q_s$ associated with the oxygen surface coverage and the donor density $N_D$ in the solid are related (figure 1.5):

\[
d_{sc} = \frac{Q_s}{N_D e}
\]

\[
\phi_s = \frac{Q_s^2}{2\varepsilon\varepsilon_0 e N_D}
\]

Typical values for $\varepsilon\varepsilon_0 \sim 10^{-12}$ $\text{F cm}^{-1}$, $N_D \sim 10^{18} - 10^{20}$ $\text{cm}^{-3}$, $\phi_s \sim 1$ $\text{V}$ imply a depletion layer thickness of $d_{sc} \sim 1 - 100$ nanometres.\textsuperscript{18,19}
In practice, an idealised thin layer free of microstructure does not exist. But the behaviour of these devices, depending on the preparation method, may be more or less influenced by the grain boundary effects within the growth structure.

![Figure 1.5. Schematic showing thin film gas sensor.](image)

While in the case of a p-type oxide, the adsorbed oxygen acts as a surface acceptor state abstracting electrons from the valence band and therefore increasing the charge carrier hole concentration at the interface. This would lead to lower resistance at the grain junction in comparison to the bulk of the material.

Materials can therefore be classified as being n- or p- type (that is, dominant carriers being electrons or holes respectively) according to whether they show a decrease or an increase in resistance (table 1.1) in response to a change in the gaseous environment.
<table>
<thead>
<tr>
<th>Material type</th>
<th>Oxidising conditions</th>
<th>Reducing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td>Resistance rise</td>
<td>Resistance fall</td>
</tr>
<tr>
<td>p-type</td>
<td>Resistance fall</td>
<td>Resistance rise</td>
</tr>
</tbody>
</table>

Table 1.1. Classification of sensor material.

Another process, which is known to modify the electronic properties of the bulk and the catalytic properties of the surface, and hence affect the gas sensing properties, is irradiation. Merdrignac et al have shown that by irradiating tin dioxide they observed a shift in the baseline resistance and the relative sensitivity to different gases has been altered.\(^{29}\)

A comprehensive model has been formulated by Yamauchi et al\(^{30}\) which included both necks and grain boundary contacts. His model represented a porous ceramic oxide structure as a large number of necks and a small number of grain boundary contacts depicted as a one-dimensional chain of particles. Three cases were used, and are differentiated according to the relative magnitude of the crystallite size (D) and twice the thickness of the space charge layer (2L) (figure 1.6).

a) D>>2L (grain boundary control). The resistance at the grain boundary contacts determines the whole resistance, because the electron channels through the necks are too wide for them to control the electrical resistance of the chain.

b) D = 2L (neck control). As necks outnumber grain boundary contacts, they determine the resistance of the whole element, hence gas sensitivity is dependent on the neck size.
c) $D<2L$ (grain control). Despite the resistivity inside each particle being smaller than that at each neck, the resistance can increase and eventually exceed that of each neck when $D$ becomes sufficiently small. Therefore the grains can control the electrical resistance and gas sensitivity when they are small.

Figure 1.6. A model set by Yamauchi et al.\textsuperscript{30} that accounts for grain size effects. Shaded parts show core region (low resistivity), while unshaded parts indicate space charge region (high resistivity). S. Yamauchi (ed.), "Chemical Sensor Technology, volume 4" Kodansha, Tokyo (1992) page30.
1.4 REACTION – DIFFUSION EFFECTS IN CERAMIC OXIDE GAS – SENSITIVE RESISTORS

As the gas diffuses through the body of a finely porous semiconducting oxide, it decomposes. This is due to the interaction with the catalytic surface of the pore and the presence of air in the background. The oxygen concentration is assumed to be constant, but the concentration of the gas and the decomposition products should vary with position inside the sensor body.\textsuperscript{31-33}

If the resistivity of the oxide changes as the concentration of the gas and decomposition products change, then the resistance of the material will vary with the position within the oxide layer.

The measured resistance is dependent on the positioning of the electrodes. Therefore, the thickness of the sensing layer, the diffusivity of the gas within the layer, the rate constant for the decomposition of the gas and the positioning of the electrodes will all affect the relative sensitivity to different gases.

Previous work in this group,\textsuperscript{34} showed that the resistance ratio $R/R_0$ of Cr$_{1.8}$Ti$_{0.2}$O$_3$ sensor responds to carbon monoxide and acetone (figure 1.7). The work also showed that there was an apparent concentration gradient for each gas since the response on the large electrode spacing was higher than that of the small electrode. The type of device used is illustrated in figure 1.8 where two pairs of electrodes are used instead of one, each pair with a different electrode separation. This provides information on the response from different regions of the film.
What is also apparent is that concentration gradient for acetone was steeper than that for carbon monoxide since the difference in response between the large and small electrodes was greater for acetone. That means that the rate of combustion of acetone on the surface of the oxide was significantly higher than that for carbon monoxide.

Figure 1.7. Experimental responses $R/R_0$ of large (—) and small (-----) electrodes to (a) carbon monoxide (b) acetone on $\text{Cr}_{1.5}\text{Ti}_{0.2}\text{O}_3$, at concentration shown in (c) and (d) respectively.\textsuperscript{34} D. E. Williams, K. F. E. Pratt, J. Chem. Soc., Faraday Trans., 92, 4497 (1996).

Williams et al\textsuperscript{35-36} have described various designs for devices with multiple electrode spacing. One example of a device which has a common electrode and three sets of electrode gaps (small, medium and large) all on one sensor is shown in figure 1.9.
CHAPTER ONE

Gas

Current lines

Oxide layer

Electrodes

Substrate

Figure 1.8. Diagram representing self-diagnostic device with two pairs of electrodes.

Figure 1.9. Self-diagnostic sensor with three gaps, small, medium and large, and the common electrode.

37
1.5 MICROSTRUCTURE

1.5.1 POLYCRYSTALLINE MATERIALS

Crystal orientation has a significant effect on the physical properties of crystalline solids. Factors like electrical conductivity, thermal expansion, elastic modulus etc. are greater in some direction through the crystal than in others. Such factors can affect the material and its application including gas sensing. However, in practice, many materials consist of a very large number of randomly oriented crystals deployed in a polycrystalline form and joined together via grain boundaries. The overall properties of the material generally take the value averaged over the crystal orientations. If the crystallite size in a polycrystalline material is very much smaller than the component dimension, then this material generally has an isotropic distribution of physical properties. There are exceptional circumstances where there is a marked anisotropy of the single crystal and there is a preferred orientation of the individual crystallites.
1.5.2 CONTROL OF MICROSTRUCTURE

As noted in section 1.3, microstructure of the solid plays a major role in determining the response of a gas sensor of the type considered here. The more porous the solid is or the smaller the grains are in size then there is more surface area for the gas to interact with the solid.\textsuperscript{19,38+39}

Microstructure may be altered by altering the particle size in the preparation, changing the sintering temperature, or introducing substances which will generate a small amount of a liquid phase at the chosen processing temperature.

Generally there is a gradual increase in the average size of a particle as the firing temperature increases. Small grains get bigger and agglomerate together. The incentive for grain growth is provided by the reduction in relative surface area of a body composed of a few large grains relative to a body that has the same amount of material but present as a large number of small grains. Grain growth is essential for controlling grain size and hence the porosity of the solid.\textsuperscript{40+41}

To achieve grain growth the solid is sintered. This is done by starting with a finely powdered material and taking the temperature up close to, but below the solidus. Taking the temperature above the solidus causes partial melting to occur and then matter is transported from one grain to another by means of the liquid phase, which is acting as a transport medium.
At sub-solidus temperatures while sintering at the initial stages, an increase in the area of inter-particle contact occurs with time. The formation of ‘necks’ between the grains, which grow thicker with time and temperature, have the effect of pulling the grains closer together. This will lead to increasing the density of the body, which will eventually lead to the shrinkage of the body, with the pores between the particles becoming smaller and losing their connectivity.

If the size of these pores can be shrunk to zero or be ‘swept out’ to the surface of the body by grain growth, then the bulk density of the body approaches the theoretical crystal density (figure 1.10).

![Figure 1.10](image)

Figure 1.10. Progressive stages of sintering (a) loosely compacted powder (b) onset of contact between grains (c) formation of a porous 3-D network of linked particles (d) formation of a solid. A. West, “Solid State Chemistry and its Applications”, John Wiley & Sons, 1996, chapter 20, page 656.

Often, sintering of a solid ceramic is controlled by the presence of small amounts of liquid phase, present as a consequence of deliberate or adventitious additions of other phases. Then, liquid and crystal surface tension properties have a significant bearing on sintering kinetics and on
succeeding slag attack. The dihedral angle, the angle in the liquid phase between two crystalline grains, is dependent on grain growth and ultimately the texture of the body (figure 1.11). A low dihedral angle gives a large amount of liquid penetration between the grains and a small amount of grain-to-grain contact (figure 1.11b). A small dihedral angle generally gives a more rapid grain growth and a larger final grain size. The initial grain size plays a major role in the kinetics of grain growth, as a fine-grained body sinters more rapidly than a coarse grained one. In practice when sintering a powder compact, considerable attention must be paid to the fine grained starting materials, with a consequent high surface area.

The dihedral angle is important in determining the strength of the material and the degree of the slag attack as well as influencing grain growth kinetics. Therefore for a solid grain to grain contact, a large dihedral angle is required (figure 1.11c).

Figure 1.11. The dihedral angle and its effect on the amount of grain-to-grain contact. A. West, “Solid State Chemistry and its Applications”, John Wiley & Sons, 1996, chapter 20, page 657.
1.6 COLLOIDAL SYSTEMS

Fine particles as the starting materials for ceramic preparation and for sensor fabrication can either be obtained by mechanical milling of powders or by chemical means. The chemical methods proceed through the production of colloidal dispersions. Surfactants may be used to stabilise these dispersions and also to prevent agglomerations when a powder is separated and dried.

Colloids are dispersions of small particles of one material in another, these particles tend to be in the order of 500 nm or less in diameter and are aggregates of numerous atoms or molecules. The reason why colloids are so important is because the ratio of surface area to their volume is so large that their properties are dominated by events at their surface.\(^{42}\)

There are two classes of colloids, the lyophilic and the lyophobic. Lyophilic colloids can be dispersed easily by adding a suitable solvent to the dry material, which will first swell as it takes up the liquid, and will finally form a homogeneous colloidal solution. On the other hand, a lyophobic colloid can only be dispersed by vigorous mechanical agitation.\(^{43}\)

A surfactant or a surface-active agent is a species that is active at the interface between two phases, such as the interface between hydrophilic and hydrophobic phases. A surfactant usually accumulates at the interface and modifies its surface tension.\(^{42}\)
1.7 PHASE RELATIONS OF THE Cr₂O₃-TiO₂ SYSTEM

Early work by Andersson et al. revealed that heating mixtures of titanium oxide and chromium oxide to 1300 – 1400 °C in an argon atmosphere resulted in mixed oxides Tiₙ₋₂Cr₂O₂ₙ₋₁ (n = 6, 7, 8 and 9). This work also showed that when these oxides were heated still further, to even higher temperatures, the structures seem to undergo a partial disordering. This was shown by obtaining powder patterns that differed in a characteristic way from the original starting material. Thus, while part of the reflections were unchanged, several appeared diffuse and with reduced intensities, while others were not even visible after the high temperature firing.

Andersson also proposed an 'ideal' cell structure, and this was based on the crystal structure of Ti₅O₉. The structure was described as being built up of slabs of a rutile-structure type, i.e. TiO₆ octahedra joined by edges and corners as in rutile structure. He also stated that the slabs are of infinite extension in two dimensions and have a characteristic finite width corresponding to five TiO₆ octahedra in a third direction, where the mutual connection of the slabs takes place by means of TiO₆ octahedra sharing faces (figure 1.12).
Work in the late seventies by Somiya et al\cite{Somiya} report phase relations in the Cr$_2$O$_3$-TiO$_2$ system at temperatures between 1400 - 1765 °C in air. The group also found that the series of Cr$_2$Ti$_{n-2}$O$_{2n-1}$ ($n = 6, 7$ and $8$) were distinct phases in this range of reaction temperature, whilst a continuous solid solution existed for the compositions of $n\geq 8$ below 1425 °C. They also reported that Cr$_2$Ti$_2$O$_7$ existed in a wide homogeneity range, which corresponds to a composition of approximately $3 < n < 5$. High temperature phases also existed above 1425 °C and seemed to be closely related to each other from the structural viewpoint, except that some X-ray diffraction lines were strongly diffused.

More recently another group lead by Venezia\cite{Venezia} confirmed that by preparing a series of samples using polycrystalline TiO$_2$ (anatase) and Cr at different atomic concentrations (0.2-5.0 at. %), prepared by a co-precipitation method, that an increase in temperature produced release of the chromium from the solid solution. At the same time, acceleration in the rate of the anatase-to-rutile phase transition was observed.

Figure 1.12. a) Unit cell of rutile with positions of metal atoms indicated. b) Interrelation of basic rutile-type structure of adjacent slabs of Ti$_2$O$_3$.\cite{Andersson}
CHAPTER TWO

EXPERIMENTAL
CHAPTER TWO
EXPERIMENTAL

2.1 GENERAL

This chapter describes the preparation of four sets of powders, the first and the fourth method being based on the decomposition of ammonium dichromate while methods two and three are based on a co-precipitation method. Other details of sensor preparation, such as firing procedure, ink preparation and screen printing are also described. The operation of the rig where the sensors are tested is also illustrated. A brief description of some of the analytical techniques used is given (table 2.1). Finally, the variability of preparation and source of errors are addressed.

<table>
<thead>
<tr>
<th>Analytical technique</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Morphology, particle size estimate</td>
</tr>
<tr>
<td>EDAX</td>
<td>Elemental analysis</td>
</tr>
<tr>
<td>EPMA</td>
<td>Quantitative elemental analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>Phase identification, crystallite size</td>
</tr>
<tr>
<td>XPS</td>
<td>Surface analysis</td>
</tr>
</tbody>
</table>

Table 2.1. Analytical techniques used and their benefits.
2.2 EQUIPMENT USED

HP5 black and white film (Ilford), was used to take photographs for SEM, and the rest of the developing and printing material including the film and paper developer stopper and fixer were supplied by Ilford.

- Firing (1000 °C): Carbolite furnace HTC 1400.
- Firing (800 °C): Carbolite furnace LMF3-PD.
- Gold coating: Edwards sputter coater S150B.
- XRD: SIEMENS D5000 X-ray diffractometer, transmission mode, incident beam monochrometer, Cu-Kα.
- XPS: VG ESCALAB 220i XL, sample pressure typically 5×10⁻¹⁰ mbar, monochromated Al-Kα source.
- Electron microprobe: JEOL Superprobe JXA-8600

2.3 POWDER PREPARATION

2.3.1 METHOD ONE

Ultra fine particles of chromium oxide were prepared by combusting ammonium dichromate \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) at 300 °C in air.⁴⁷,⁴⁸

\[(\text{NH}_4)_2\text{Cr}_2\text{O}_7 + \text{Heat} \Rightarrow \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + \text{N}_2\]

(Bright Orange) (Green)
Stoichiometric amounts of chromium oxide and commercial titanium dioxide (>99% purity, <5μm particle size, Aldrich) were mixed thoroughly together in an industrial blender using acetone as a solvent.

The acetone was then evaporated using a rotary evaporator with the aid of an ultrasonic bath, and the resulting powder was fired in the furnace to the desired temperature.

2.3.2 METHOD TWO

Hydrated chromium oxide was prepared by dissolving 25 grams of Cr(NO$_3$)$_3$.9(H$_2$O) (deep blue) in 180 ml of distilled water; 25 ml of ammonia solution (sp. gr. = 0.88) was added to the initial solution, which gave a colloidal suspension of ultra fine, light green particles of hydrous chromium oxide.

Hydrated titanium dioxide was prepared by adding a stoichiometric amount (the amount required to reach the target stoichiometry of chromium titanium oxide) of Ti[OCH(CH$_3$)$_2$]$_4$ very slowly to 40 ml of isopropyl alcohol in an inert atmosphere. The mixture was added to 100 ml of acidified water (pH 1.5). The solution was precipitated using 30 ml of ammonia (sp. gr. = 0.88) to give a white colloid.$^{49-53}$

Both chromium oxide and titanium oxide colloids were washed with distilled water several times and centrifuged. The resultant solids were mixed thoroughly in water using a high-speed mixer (homogeniser) for one hour. The suspension was then dried using a rotary evaporator with the aid of an ultrasonic bath to help keep the particles constantly dispersed. The oxide was subsequently fired in the furnace to the desired temperature.
2.3.3 METHOD THREE

The preparation procedure for the third method was exactly as method two, except for the final stage of the preparation, where one gram of surfactant and half a gram of terpineol were added to the colloids before they were mixed in the homogeniser and subsequently dried using a rotary evaporator and an ultrasonic bath. The aim of the addition was to prevent agglomeration of the powder during drying. Finally the powder was fired in the furnace to the desired temperature.

2.3.4 METHOD FOUR

The Cr$_2$O$_3$ preparation procedure for method four is exactly as method one. Except that, for the TiO$_2$, a colloidal suspension prepared as in method two was added to a water suspension of the chromium oxide. Only one stoichiometry (Cr$_{1.8}$Ti$_{0.2}$O$_3$) was made this way. The sintered powders were pressed into 13 mm diameter pellets and not made into sensors as in the first three methods. The same amount (0.75 grams) of powder was used for all the pellets and they were pressed under 1 ton for about 15 seconds.

2.3.5 STANDARD PREPARATION FOR EPMA

The preparation of standards was done in order to establish a calibration curve for both chromium and titanium. This should give an accurate result because the electron beam samples a volume much larger than the average particle size, therefore particle-to-particle variations are averaged out in the process.
The standards for all the stoichiometries used were prepared. Cr$_2$O$_3$ (Aldrich) and TiO$_2$ (Aldrich), were mixed in acetone for 24 hours using a ball mill. The powders were then dried in a rotary evaporator and subsequently fired in the furnace at 1000 °C for one hour. The powders were pressed into a pellet and carbon coated in order to perform EPMA analysis on them. Standards were prepared in this way in order to provide known materials which matched the sensor materials as closely as possible with respect to the matrix and the density.

To assess the accuracy of the EPMA method, the composition of the standards were determined by comparison with pure metal standards, applying correction assuming fully dense material. As can be seen from table 2.2, the target and analysed compositions were very similar for both chromium and titanium. In order to establish the margin of error, the target composition was plotted against the EPMA-analysed composition. After performing a regression on the result it was found the overall error was approximately ±0.4% (figure 2.1). This means that, despite the difference in matrix, the metallic standards could be used satisfactorily to determine composition. This is what has been done for all analysis subsequently reported in this thesis.

<table>
<thead>
<tr>
<th>Target composition</th>
<th>Target composition</th>
<th>Analysed composition</th>
<th>Analysed composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>100*Cr/(Ti+Cr)</td>
<td>100*Ti/(Ti+Cr)</td>
<td>100*Cr/(Ti+Cr)</td>
<td>100*Ti/(Ti+Cr)</td>
</tr>
<tr>
<td>89.0</td>
<td>11.0</td>
<td>89.4</td>
<td>10.6</td>
</tr>
<tr>
<td>92.0</td>
<td>8.0</td>
<td>92.4</td>
<td>7.6</td>
</tr>
<tr>
<td>93.5</td>
<td>6.5</td>
<td>93.7</td>
<td>6.3</td>
</tr>
<tr>
<td>96.0</td>
<td>4.0</td>
<td>96.3</td>
<td>3.7</td>
</tr>
<tr>
<td>97.5</td>
<td>2.5</td>
<td>97.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 2.2. Target and EPMA analysed composition of standard.
Figure 2.1. Regression of chromium and titanium standards as a function of the target composition. Composition expressed as Cr/Cr+Ti and Ti/Cr+Ti %.
2.4 POWDER SINTERING

The powder was fired in a computer controlled muffle furnace. The sintering program was a slow (5 °C/min.) temperature ramp to 400 °C, followed by a more rapid ramp (15 °C/min.) to the desired temperature. That temperature was held for a length of time depending on the experiment the furnace was then switched off and allowed to cool to room temperature before the specimen was removed. The sample crucible was covered by another crucible and both were made of re-crystallised high purity (99.8%) alumina, which was of high resistance to chemical attack. This was in order to avoid any cross contamination from the inside of the furnace with the sample, due to some early problems encountered where small (<1%) amounts of silicon were detected and thought to come from the furnace elements. This problem was eliminated when the sample crucible was covered by another one.

The accuracy with which the ramp was actually followed in the furnace was good to up to about 800 °C after which it was difficult for the furnace to maintain 15 °C/min. The actual temperature at the sample was usually about 50 °C lower than the registered temperature, this was checked using a thermocouple inserted near the sample crucible. It took about 15-30 minutes for the furnace to reach that temperature during the dwelling time especially when the furnace was programmed to high temperature (>1000 °C). On cooling, the temperature fell to ~400 °C within about 45 minutes. This problem with the inaccuracy of the furnace is systematic error that is present for all the samples.
2.5 INK PREPARATION

Ink was prepared by mixing a 1 to 1 ratio by weight of the fired powder to the vehicle. The vehicle was prepared by mixing a 9 to 1 ratio by weight of commercial vehicle (400 Vehicle)** to surfactant (Triton X-100). The powder and the vehicle were mixed initially by hand, and then passed through a triple roll mill to obtain a very smooth and consistent ink. The exact composition of the commercial vehicle was unknown. However, such materials typically comprise a polymer such as cellulose acetate together with high and low boiling point solvents such as mixtures of terpineol and ethylene glycol diacetate.

2.6 SCREEN PRINTING

Seven layers of ink (∼15 μm per layer), were printed on to an alumina substrate (3*3 mm). After each layer was printed, the substrate was dried under an infrared light for 20 minutes. The sensors were subsequently fired in the furnace in order to obtain good attachment between the oxide layers and the substrate. The final stage after screen printing was spot welding of the sensor on to a header, after which the sensor was ready for testing in the gas rig.

2.7 FIRING OF SENSORS

All the sensors were fired after they had been screen printed, in order to decompose the vehicle and strengthen the attachment of the oxide to the gold electrodes and the substrate.

** ESL EUROPE, 8 Commercial Road, Reading, Berkshire, England, UK.
The sensors were fired slowly (10 °C/min.) to the desired temperature (depending on experiment) and held at that temperature for two hours.

2.8 GAS RIG EXPERIMENTS

All the gas experiments were conducted in one gas rig. The apparatus that held the sensors was made up of a long Pyrex glass tube with six SQ28 fittings, which acted as sensor ports (figure 2.2). Concentrated gas and the air diluent (laboratory compressed air, filtered, scrubbed of CO$_2$ and dried) were fed separately into the base of the apparatus through diametrically opposed ports. The overall flow rate of the experiments was usually 200 cm$^3$ min$^{-1}$.

In humidity experiments, the relative humidity was controlled by passing a portion of the air stream through distilled water at room temperature and mixing the wet and dry streams before introducing them into the apparatus.

A voltage was applied by a heater driver box across the platinum heater track on the back of the sensor so as to raise and control the temperature of the device. The change in resistance of the semiconducting oxide powder, between the gold electrodes was monitored by a Keithly auto-ranging digital multimeter. This system used a Wheatstone bridge arrangement to control the heater at constant resistance and hence constant temperature. As we can see from figure 2.3 there are four resistors with typical values of $R_a = 3.3$ kΩ, $R_b = 0-20$ Ω, $R_c = 3.3$ kΩ and $R_h = 0-20$ Ω.

The ratio

$$\frac{R_a}{R_b} = \frac{R_c}{R_h}$$
Therefore by controlling the variable resistor $R_y$ we are able to control the resistance of the heater $R_h$. As this circuit uses an operational amplifier to keep the ratio between the resistors constant, the margin of error is usually in the order of about 1 millivolt, which corresponds to about $\pm 3^\circ C$ in heater temperature.

For each experiment the computer was programmed with a gas and a heater program. The gas program controls both the solenoid valves and the mass flow controllers (Tylan). The computer not only controls amount of gas flowing and the temperature but also acts as a data logging device, in which all the data are fed back into the computer via an IEEE board and recorded separately for each device.

![Figure 2.2](image)

Figure 2.2. All glass apparatus for the study of gas response of multiple self-heated sensor elements.\textsuperscript{54} D. H. Dawson and D. E. Williams, J. Mater. Chem., 6 (3), 409-414 (1996)
A typical experiment usually lasted for two hours, starting with 30 minutes of air to establish a stable base line followed by a high concentration pulse of the tested gas (example; 1000 ppm CO, 10 ppm acetone, 100 ppm ammonia, 10 ppm ethanol, etc.). The gas concentration was then halved several times before the gas was switched off. The original base line was normally recovered (figure 2.4).

The response, $S$, of the sensor is defined here as:

$$S = \frac{R\text{ (gas)}}{R\text{ (air)}}$$

Where $R\text{ (gas)}$ is the final resistance in each concentration and $R\text{(air)}$ is the resistance of the sensor in pure air after stabilising.
Figure 2.4. Typical gas response trace, showing the variation in resistance with gas concentration (1000, 500, 250 and 125 ppm) for carbon monoxide in dry air at 350 °C operating temperature for powder prepared by method one [Ti/(Ti+Cr) = 5.34%].
2.9 ANALYTICAL TECHNIQUES

2.9.1 GENERAL

The powders prepared were checked by X-ray powder diffraction to show that they formed a solid solution. The powder pattern of some samples was used to estimate crystallite size using the Scherrer equation (section 2.9.5). Scanning Electron Microscopy (SEM) was used to study the microstructure of the solids and to estimate the particle size of different powders from the images produced. Elemental analysis of the sample were obtained by using the Energy Dispersive Analysis of X-rays (EDAX) method on the SEM. More accurate measurements using wavelength-dispersive spectrometers were performed on the electron microprobe.
2.9.2 SCANNING ELECTRON MICROSCOPY

The principal technique used here for studying texture, topography and surface features of powders or solid pieces was scanning electron microscopy (SEM). SEM is an extremely versatile technique capable of giving structural information over a wide range of magnifications. The primary reason for SEM’s usefulness is first the high resolution that can be obtained when objects are examined, values on the order of 2-5 nm being obtainable while advanced instruments can achieve resolution of better than 1 nm, and second because of the large depth of focus of the instrument the resulting pictures have three-dimensional quality.55-58

The electron column of an SEM machine usually consists of an electron gun and two or more electron lenses operating in vacuum. The electron gun produces a source of electrons that are accelerated to an energy in the range of 1-40 keV. The electrons are focused to a small spot of about 50 to 100 Å in diameter on the surface of the sample. The electron beam is scanned systematically over the sample. Both X-rays and secondary electrons are emitted by the sample. The former are used for chemical analysis and the latter are used to build up an image of the sample surface which is displayed on the screen (figure 2.5).
The design of electron microscope used in these experiments was of the reflective type. It is necessary to coat the sample with a thin layer of a metal (gold), especially as the sample is a semiconductor in order to prevent the build up of charge on the surface of the sample. The sample was placed on a stub which was covered with carbon tape and then quick drying silver paint was used on the side of the sample to help connect the two conducting layers on the top (gold) and the bottom (carbon). The sample was then placed in the vacuum chamber and was focused in using the upper detector (not more than 1 millimetre from the lens) which had a significantly higher resolution then the lower one.

Some problems were initially encountered like the build-up of charge on the specimen, which gave a highly distorted image. This was resolved by coating the samples for longer periods of time (five minutes) with gold, which resulted in a higher quality image. Carbon coating did not give as good quality image as the gold, therefore gold was used in nearly all the specimens tested.
2.9.3 ENERGY DISPERSIVE ANALYSIS OF X-RAYS

The X-rays emitted on electron bombardment in the SEM are characteristic emission spectra of the elements present in the sample. By scanning either the wavelength or the energy of the emitted X-rays it is possible to identify the elements present. A quantitative elemental analysis may also be made if certain calibration procedures have been adopted. The interaction volume of the electron beam with the sample determines both the lateral resolution and the depth of analysis. This is normally a function of the primary beam energy but it is invariably in the order of one micrometer. For porous specimens it is larger.

The sample was prepared in the same way as for the SEM, except for the coating where carbon was used instead of gold. This is due the fact that the gold gives a signal, which usually causes confusion and overlaps with the other signals in the region of interest.

Unfortunately, the SEM instrument that was used is limited in its ability to attain accurate quantitative analysis even after calibrations were made, therefore it was not used for quantitative analysis. But it was good at informing the presence of minor elements even at low concentrations.
2.9.4 ELECTRON PROBE MICROANALYSER

The main reason for the EPMA's usefulness is that the compositional information can be obtained from the sample using characteristic X-ray lines. The sample is analysed non-destructively, and quantitative analysis can be obtained in many cases with an accuracy of the order of 1–2% of the amount present for a given element.

The design of the electron spectrometers means that energy dispersive analysis is usually limited in sensitivity in an EPMA instrument. But the wavelength dispersive analysis where the X-rays are reflected off a crystal oriented at the correct Bragg angle for the desired wavelength is much more efficient, therefore higher sensitivity is achieved. The instrument is designed to have much better stability of the electron gun and optics than an SEM, but not necessarily the highest spatial resolution.

For examination of a cross section, the sensors were put in an epoxy resin mould and subsequently cross-sectioned in the desired location. The samples were polished down using various degrees of diamond paste (25, 6, 3, 0.25 μm), in order to achieve a very clean and flat surface which was crucial for the instrument to operate satisfactorily. The use of diamond paste avoided smearing of gold across the oxide. The samples were then carbon coated and put on a stub which had a carbon tape applied on the top surface. Quick drying silver paint was used on the side of the sample in order to connect the top surface of the sample with the base, so as to prevent the build-up of charge on the surface. Metallic standards were used for each of the elements measured. These standards had to be polished in order to achieve a flat and clean surface.
A typical example of an EPMA map is given in figure 2.6, it shows an area of $100 \times 100 \, \mu\text{m}$ with two small electrodes in the middle, chromium titanium oxide on the top and the alumina substrate on the bottom of the map.

![Figure 2.6. Typical EPMA map of a sectioned gas sensor.](image)

An SEM micrograph of a sectioned sensor is given in figure 2.7. It shows the alumina substrate on the bottom, a section through the small electrode in the middle and the chromium titanium oxide layer on the top of the micrograph.
Figure 2.7. SEM micrograph of a sectioned gas sensor.
2.9.5 X-RAY POWDER DIFFRACTION (XRD)

For every given substance there is an XRD pattern, which is a set of lines or peaks each of different intensity or position. Crystals are built up in planes such as each one acts as a slit. Some of the X-rays are reflected off a plane where the angle of reflection equal to the angle of incidence, but some are transmitted to be reflected by succeeding planes. As can be seen from figure 2.8, two X-ray beams 1 and 2 are reflected from adjacent planes, A and B within the crystal. An extra distance of xyz has to be travelled by beam 2 as compared with beam 1, and for 1 and 2 to be in phase, distance xyz must equal a whole number of wavelengths. The perpendicular distance between pairs of adjacent planes, the d spacing, d, and the angle of incidence, Bragg angle, θ, are related to the distance xy by

\[ xy = yz = d \sin \theta \]

Thus \[ xyz = 2d \sin \theta \]

But \[ xyz = n\lambda \]

Therefore \[ 2d \sin \theta = n\lambda \quad \text{Bragg's law} \]

Figure 2.8. Bragg's law for X-ray diffraction. A. West, Solid State Chemistry and its Application, John Wiley & Sons (1996), page 122.
The positioning of the lines are fixed and are characteristic of that particular substance while the intensities vary somewhat from sample to sample depending on the instrumental conditions and the method of sample preparation. By observing the line positioning and a semi-quantitative consideration of line intensities it is usually possible to identify a sample.\(^{40,59}\)

Phase identification is one of XRD's applications, where the diffraction pattern is identified by comparing it to standard pattern in the data base. Mixtures of substances can be identified as long as the patterns are available for comparison. Quantitative phase analysis can also be made by XRD, but it is necessary to add an internal standard which has a well-crystallised phase such as KCl (10%), where a line in the powder pattern of the phase of interest is chosen and its intensity is compared with that of an internal standard line.

Another application is crystallite size measurements, provided that the average crystal size is less than about 2000 Å. The broadness of the lines increases with decreasing crystallite size, the limit being reached when the particle diameter is roughly 20-100 Å. At this point the lines become so broad that they effectively 'disappear' into the background radiation.

The formula for crystallite size broadening is the Scherrer formula:

\[
t = \frac{0.9 \lambda}{B \cos \theta_B}
\]

Where:

. \(t\) is the thickness of the crystal in angstroms
. \(\lambda\) is the X-ray wavelength in Angstroms
. \(\theta_B\) the Bragg angle in degrees
The line broadening $B$, is measured from the extra peak width at half the peak height and is obtained from the Warren formula:

$$B^2 = B^2_M - B^2_S$$

Where $B_M$ is the measured peak width in radians at half peak height and $B_S$ is the corresponding width of a peak of a standard material, mixed in with the sample, whose crystallite size is considerably greater than 2000Å and which has a diffraction peak near to the relevant peak of the sample. In this way, the intrinsic broadening caused by small size is deconvoluted from the broadening imposed by the instrument resolution.

The sample was prepared by grinding together about 20 milligrams of the powder in question with 10% in weight of the KCl standard using a pestle and mortar. The powder was then applied onto a piece of Scotch tape, which is amorphous; another piece of Scotch tape was applied on top of the first one to keep the sample in place. The instrument used an incident beam monochromator and operated in transmission mode. In order to obtain a complete high quality powder pattern required a run for a long period of time (~12 hours). Therefore, a small part of the spectrum was chosen ($\theta = 23.5 - 29$) which contained a chromium oxide, titanium dioxide and a KCl (reference) peak all in that region. The measurement time was reduced to about 1.5 hours. Unfortunately, that means we are relying on this small window to observe any phase changes that occur in the powders and not the full pattern. Several random experiments were performed, and a full high quality diffraction pattern was obtained that confirmed the result of the partial pattern. An example of this is shown in figure 2.9, where a full diffraction pattern was run on three samples ($Cr_2O_3$ (Aldrich), $Ti/(Ti+Cr) = 10.63\%$, $Ti/(Ti+Cr) = 5.34\%$ method four), and as we can see there is virtually no peak shift in all three samples for the KCl standard and the chromia peaks. This was done in order to judge the stability of the instrument calibration from one experiment to the next.
Composition:

Point 1. \( \text{Cr}_2\text{O}_3 \)
Point 2. \( \text{Ti}/(\text{Cr}+\text{Ti}) = 10.63\% \)
Point 3. \( \text{Ti}/(\text{Cr}+\text{Ti}) = 5.34 \% \)

Figure 2.9. X-ray powder diffraction data for \( \text{Cr}_2\text{O}_3 \) (Aldrich), \( \text{Ti}/(\text{Ti}+\text{Cr}) = 10.63\% \) and \( \text{Ti}/(\text{Ti}+\text{Cr})=5.34\% \) both prepared by method four.
2.9.6 X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) is a method for analysing surface species, where the analysis depth is usually in the order of about three atomic layers. In XPS, the technique is to measure the kinetic energy of the electrons that are emitted from matter as a consequence of bombarding it with photons. If the incident photon has sufficient energy (hv) it is able to cause photoelectron emission: absorption of the photon causes an electron which was bound to the solid with energy \( E_B \) to be ejected into the vacuum with kinetic energy \( E_K \).

\[
E_K = hv - E_B
\]

If the incident radiation is monochromatic and of known energy, and if \( E_K \) can be measured using an electron energy analyser, then the binding energy \( E_B \) can be deduced (figure 2.10).  

![Figure 2.10](image)

Figure 2.10. A one electron energy level diagram.\(^{60}\) M. Prutton, Introduction to Surface Physics, Oxford Science Publications, Clarendon Press, Oxford, 1994. Page 16.
The choice of anode material for XPS is determined by the energy of the X-ray transition generated. It must be of high enough photon energy to excite an intense photoelectron peak from all elements of the periodic table, with the exception of the very lightest. The most popular anode materials in XPS are aluminium or magnesium. Alternatively, X-rays may be used from a synchrotron radiation source which has the added advantage of being very bright and, in combination with a monochromator, can be tuned to the X-ray energy of interest.

The XPS machine that was used incorporated a monochromated Al-K$_\alpha$ source. The analyser used a step size of 600.109 meV and the pressure inside the chamber was typically $5 \times 10^{-10}$ mbar. The sample was prepared by simply applying the sensor onto an aluminium stub that was covered with carbon taped to aid adhesion, the sample was then covered with a silver foil to help reduce the excess of charge on the surface of the sample. The machine was regularly re-calibrated with a standard in order to eliminate any peak drift that might occur. The atomic quantification was done automatically by the machine by calculating the area under the curve of the relevant peak. A typical example of an XPS spectrum is shown in figure 2.11.
Figure 2.11. Typical example of an XPS spectrum. The powder was prepared by method one \[\% (\text{Ti}+\text{Cr}) = 10.63\%\].
2.10 EXPERIMENTAL ERROR

As can be seen from the experimental procedure, each one of these sensors goes through several processes before it is ready for testing and each stage will accumulate an error with it.

At the start the substrates that are used have gold tracks for the electrodes, and this gold that is used usually has various bonding agents that diffuse out of the gold to the oxide layer when it is heated. There is also the electrode gap that is laser scribed, which is not always consistent from sensor to sensor.

There are also the powders, especially the ones that are prepared in the co-precipitation method which do not always give the stoichiometric amounts that are expected because the reactants do not precipitate at the same rate, the solutions are supersaturated or the two reactants have different solubilities. To make comparisons of response of sensor with composition, accurate elemental analysis on the electron microprobe was required.

There are also other problems like the consistency of the ink from one batch to the next, the thickness of the oxide layer and the actual temperature of the powder as the furnace temperature is ramped-up slowly to the desired setting.

These potential problems were addressed by adopting a procedure as consistent as possible from one preparation to the next: by using the same type and amount of vehicle and surfactant, using the same muffle furnace and the same firing regime for all powders. As will be seen, repeatability between different devices using the same procedure was ±6.5%.
2.11 VARIABILITY EXPERIMENTS

2.11.1 GENERAL

These experiments were conducted in order to see if there was any variability in the response of the devices from one sensor to the next. One batch of powder was prepared using method one and had a theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$. The powder was sintered at 1000 $^\circ$C for one hour and then screen printed on to the substrate and subsequently fired at 700 $^\circ$C for two hours to decompose the vehicle. Hence, all the sensors had the same composition and were sintered at the same firing temperature and should give the same response. These experiments was operated at 350 $^\circ$C.

2.11.2 GAS RIG EXPERIMENTS

As we can see from figure 2.12, the response on all five sensors for each test gases is virtually identical with a maximum error of ±6.5 % for the carbon monoxide gas while the other three gases had a much smaller margin of error. This is a small error considering the number of processes that each one of the sensors goes through before it is finally in full operation.

As for the concentration gradient, which is the variation of gas concentration through the oxide film (figure 2.13), there is virtually no variation between the devices for each test gas, with ethanol, ammonia and relative humidity showing no concentration gradient and carbon monoxide showing reverse sensitivity gradient.
Figure 2.12. Response of five identical devices prepared using method one \([\text{Ti}/(\text{Ti}+\text{Cr}) = 5.34\%]\) operated at 350 \(^{\circ}\)C.
Figure 2.13. Concentration gradient of five identical devices prepared using method one [Ti/(Ti+Cr) = 5.34%] operated at 350 °C.
2.11.3 BASE LINE RESISTANCE SHIFT

As we can see from figure 2.14 the base line resistance is virtually identical on all three electrode gaps (small, medium and large) and for all the sensors tested.

Figure 2.14. Base line resistance variation for all devices tested. Method one \([\text{Ti}/(\text{Ti}+\text{Cr}) = 5.34\%]\) operated at 350 °C.
CHAPTER THREE

PHYSICOCHEMICAL PROPERTIES OF CHROMIUM TITANIUM OXIDE
3.1 METHOD ONE

3.1.1 GENERAL

In solid state reactions, normally, the reactants are mixed together manually or mechanically and the rate of reaction will depend on the size of the particles of the reactants, the degree of homogenisation of the sample, contact between the grains and the firing time and temperature.\(^{40}\)

The decomposition of ammonium dichromate yields ultra fine particles of chromium oxide, which is very important as a starting point for the reaction, so as to increase the rate of reaction between chromium and titanium oxides. This will lead to less firing time and temperature, which will keep the particle size relatively small and the number of agglomerations less.
3.1.2 SAMPLE PREPARATION

Four sensors were prepared using Cr₂O₃ (made from the decomposition of ammonium dichromate) and commercial TiO₂ in stoichiometric amount. The powders had a theoretical composition of CrₓTi₂₋ₓO₃ (x=1.6, 1.7, 1.8 and 1.9). The initial powders were fired for one hour at 1000 °C, and they were subsequently fired, after screen printing of the ink, at 700 °C for two hours. The sintering procedure was kept constant for all sensors in-order to observe compositional effects on the response of the sensors. As noted in chapter two, the actual temperature-time profile during the firing meant that the final temperature achieved was ~950 °C, maintained for ~45 minutes. This was determined using a thermocouple which was inserted inside the furnace near the crucible.

3.1.3 ELECTRON MICROPROBE STUDIES

These studies were made in order to establish the bulk stoichiometry of the oxide powder. The analysis was made on an imaginary grid of about 50 x 50 μm and the numbers were averaged to give ratios of chromium and titanium (table 3.1). The preparation of standards and the assumptions underlying the analysis were presented in chapter two.

An electron map of the sample showed that although the majority of the sample had a single phase, there were a small number of very small-unreacted lumps of TiO₂. This is probably due to two factors: first, although the smallest grain size of commercial TiO₂ available was used, the grain size was in the order of one micrometer according to the particle size analysis data. This is larger than the Cr₂O₃ grains by about a factor of ten. This large factor will cause a problem during the firing process and invariably there will be small lumps of unreacted TiO₂. The second factor
is that firing time was probably too short (one hour), and longer time is needed in order to get full reaction and a solid solution.

<table>
<thead>
<tr>
<th>Code for Target Stoichiometry</th>
<th>Ti/(Ti+Cr) mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti40</td>
<td>10.63</td>
</tr>
<tr>
<td>Ti30</td>
<td>7.53</td>
</tr>
<tr>
<td>Ti20</td>
<td>5.34</td>
</tr>
<tr>
<td>Ti10</td>
<td>2.62</td>
</tr>
</tbody>
</table>

Table 3.1. Measured oxide ratios of powders prepared using method one and sintered at 1000 °C for one hour.

XPS was performed on all four sensors. Quantitative analysis on the surface showed that there was no change in oxygen concentration across the series, as expected (figure 3.1); this determination served to quantify the errors in the analysis. As for the Ti/(Ti+Cr)% ratio on the surface of the oxide, it showed an increase as the actual composition Ti/(Ti+Cr)% increased from 2.62 to 10.63%. These variations in the chromium and titanium concentrations on the surface are expected and are attributed to the variation in the stoichiometry of the initial powders.

### 3.1.4 BULK VS. SURFACE COMPOSITION

Figure 3.2 shows bulk and surface concentration for chromium and titanium as a function of bulk composition. A segregation of titanium to the surface is clearly demonstrated, which increases as the proportion of titanium in the bulk decreases. At the lowest concentration of titanium studied, the surface was enriched in titanium by a factor of few times in comparison with the bulk. Even so, in all cases the majority of surface cations were chromium.
Figure 3.1 XPS data showing amount of chromium, titanium, oxygen and Ti/(Ti+Cr)% on the surface as a function of composition for powders prepared using method one.
Figure 3.2. Surface / bulk comparison for titanium and chromium across the series for preparation method one.
3.1.5 X-RAY DIFFRACTION STUDIES

The XRD pattern that was obtained for all the powders was run for a small window (2θ = 23.5 ⇒ 29.0), because this window contained all of the peaks in question (Cr₂O₃, TiO₂ and the KCl standard). And as the window was small, we were able to run the machine for longer in order to obtain a high quality diffraction pattern.

As we can see from figure 3.3, all four powders show a signal at the Cr₂O₃ position and this signal increases in intensity as we go from Ti40 to Ti10 in the series. This semi-quantitative result is expected due the increase in the amount of chromium oxide across the series.

The diffraction pattern shows no signal for titanium oxide, which could indeed be due to the formation of a solid solution between chromium and titanium oxide. Another explanation for the absence of the TiO₂ signal is the fact that it is only present in very small concentrations, and that is beyond the capability of the machine to detect. So we have to rely on the electron microprobe results to establish whether a solid solution has formed.

By using the Scherrer formula for line broadening and the KCl standard line θ≈28.3 we can estimate the crystallite size. As seen from table 3.2 there was very little variation in crystallite size between the powders, which is expected as all powders were prepared using the same method and the same firing temperature and time. A more important factor is that there was no evident shift in the chromium oxide peak position in the XRD pattern for all four samples across the series, as this might inform us about the degree of reaction between the different powders.
Figure 3.3. XRD pattern for all four samples prepared using method one.
<table>
<thead>
<tr>
<th>Target Code</th>
<th>Crystallite Size /μm</th>
<th>Peak Position of Cr₂O₃, 2θ/degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti40</td>
<td>0.12 ± 0.05</td>
<td>24.49</td>
</tr>
<tr>
<td>Ti30</td>
<td>0.11 ± 0.05</td>
<td>24.50</td>
</tr>
<tr>
<td>Ti20</td>
<td>0.11 ± 0.05</td>
<td>24.50</td>
</tr>
<tr>
<td>Ti10</td>
<td>0.12 ± 0.05</td>
<td>24.51</td>
</tr>
</tbody>
</table>

Table 3.2. XRD data showing crystallite size and peak position of samples prepared using method one and fired at 1000 °C for one hour.
3.1.6 SCANNING ELECTRON MICROSCOPY STUDIES

SEM is an extremely useful technique because it not only shows the size of the individual grains but it also shows how these grains interact with each other to form anything between an agglomerated cluster to a highly uniform powder.

As we see from figure 3.4 all four powders showed the same grain structure with grain size of about 100 - 150 nanometres, which confirms the XRD results. This means that each one of these grains was a single crystallite. These small grains or crystallites were gathered in small to medium size clusters of about 500 nanometres across.

There was very little difference in the microstructure between these powders, all showing a degree of porosity and small clusters of grains. This is what is expected as all the powders were prepared using the same method and the same firing temperature and time. Therefore the variation in microstructure should be small enough to have only a very small effect on the response of these sensors.
Figure 3.4. SEM micrographs for Ti/(Ti+Cr) mol\% = a) 10.63, b) 7.53 c) 5.34 and d) 2.62\% samples prepared using method one.
3.2 METHOD TWO

3.2.1 GENERAL

This method was developed to overcome the problem of the large particle size of titanium oxide, which may lead to some unreacted lumps of TiO$_2$ in the powder mixture.

The co-precipitation method can usually help in reducing the size of the particles and help in achieving a high degree of homogenisation and hence help in speeding-up of the rate of reaction. This usually reduces the need for prolonged periods of firing which help in reducing the number of agglomerations between the particles. Unfortunately, this method does not always work and is often not suitable for accurately stoichiometric phases.

The length of time the powder is fired and the temperature that it is fired at, also controls the rate of reaction of the oxide, and consequently, this will lead to a better understanding of the conditions that are needed to obtain a solid solution.
3.2.2 SAMPLE PREPARATION

Two groups of sensors were prepared using method two. First, a series of four sets of CTO sensors were prepared using the co-precipitation method, Cr$_x$Ti$_{2-x}$O$_3$ (target, x=1.6, 1.7, 1.8 and 1.9). Each set had three sensors that were fired at 800, 900 and 1000 °C for one hour. Hence, there were a total of 12 sensors for the series.

The second group consisted of five sensors all with a target composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$ fired at 1000 °C for 15 minutes, 1, 4, 12 hours and 1200 °C for 12 hours.

These firing times and temperatures were chosen to see the differences (if any) in morphology of the solid and the variation in response between the sensors when they are tested towards certain gases.

3.2.2.1.1 ELECTRON MICROPROBE STUDIES

Table 3.3 gives the electron microprobe data. The actual composition obtained was significantly different to the target composition, having less titanium than projected.

This variation is due to the way that these powders were prepared, in a series of steps in each of which material could be lost.
<table>
<thead>
<tr>
<th>Target Code</th>
<th>Ti/(Ti+Cr) mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti40</td>
<td>6.40</td>
</tr>
<tr>
<td>Ti30</td>
<td>4.42</td>
</tr>
<tr>
<td>Ti20</td>
<td>1.15</td>
</tr>
<tr>
<td>Ti10</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 3.3. Measured oxide ratios of powders prepared using method two (fired at 1000 °C for one hour).
Quantitative XPS analysis was performed on all samples. The variation in oxygen concentration was used to check the error in the analysis, the main source of error in the measurement being the amount of carbon on the surface. Results from figure 3.5 show an increase in the amount of titanium on the surface as we go from actual composition Ti/(Ti+Cr)% 0.33 to 6.40% across the series. The amount of titanium increased with increase in firing temperature of the oxide from 800 to 1000 °C, which means there was titanium segregated out to the surface of the grain as the firing temperature was increased for a given composition.

As for the chromium, there was a decrease in surface concentration across the series from Ti/(Ti+Cr)% 0.33 to 6.40% for a given firing temperature (figure 3.5). For a given composition, the amount of chromium on the surface decreased with increase of firing temperature from 800 to 1000 °C. There was no significant variation in oxygen concentration on the surface of all the samples tested for all given compositions and firing temperatures (figure 3.5).
Figure 3.5. XPS surface analysis data for titanium, chromium, oxygen and Ti/(Ti+Cr) ratio on the surface for a series of compositions sintered at 800, 900 and 1000 °C, for samples prepared by method two.
3.2.2.1.3 BULK VS. SURFACE COMPOSITION

The extent of surface segregation can be gauged from the Ti/(Ti+Cr) ratio on the surface. This decreased across the series for a given firing temperature as the bulk titanium content decreased (figure 3.5). The extent of segregation increased with increase of the firing temperature from 800 to 1000 °C for a given composition. Thus it appears that the titanium segregated out to the surface of the oxide as the firing temperature increased.

Figure 3.6 shows significantly more titanium segregating on to the surface compared to the bulk, for the samples that were fired at 1000 °C for one hour. As for the chromium the opposite was true: there was more in the bulk compared to the surface for a given composition. It is also notable that the segregation ratio \( \frac{\text{Ti}/(\text{Ti+Cr}) \text{on the surface}}{\text{Ti}/(\text{Ti+Cr}) \text{in the bulk}} \) was higher for this preparation method than for method one.

3.2.2.1.4 X-RAY DIFFRACTION STUDIES

All samples exhibited a similar XRD pattern to that of Ti30 figure 3.7, which showed that the initial unfired sample had only a flat base-line, due to the very small particle size of the unreacted \( \text{Cr}_2\text{O}_3 \) given very broad peaks. The samples that were fired at 800, 900 and 1000 °C show a progressive sharpening of the \( \text{Cr}_2\text{O}_3 \) peak at \( \theta \approx 24.5 \), with no apparent peak for \( \text{TiO}_2 \).
There was also a small apparent Cr$_2$O$_3$ peak shift (figure 3.8), with 2-theta shifted towards higher values as the firing temperature increased from 800 to 1000 $^\circ$C. This was apparent for all powders and it can either be taken as an indication of how complete the reaction is between chromium and titanium oxide or it might be a consequence of loss of residual water from the lattice. Figure 3.9 shows the increase of crystallite size estimated using the Scherrer formula as the firing temperature was increased from 800 to 1000 $^\circ$C. This was expected due to increase in crystal growth as the firing temperature was increased for a given length of time. The crystallite sizes were significantly smaller than that found for method one. This result was mirrored on all four sets of samples.
Figure 3.6 Surface bulk comparison for various composition sintered at 1000 °C for one hour prepared by method two.
Figure 3.7. XRD pattern of Ti/(Ti+C)=4.42% powder, prepared by method two, sintered at 800, 900, and 1000°C and the unreacted powder.
Figure 3.8. Cr$_2$O$_3$ peak shift as a function of sintering temperature (800, 900 and 1000 $^\circ$C) for powders prepared by method two.

Figure 3.9. Crystallite size of oxide powders prepared using method two and sintered at 800, 900 and 1000 $^\circ$C, estimated using Scherrer equation.
3.2.2.1.5 SCANNING ELECTRON MICROSCOPY STUDIES

As can be seen from figure 3.10, both Ti/(Ti+Cr) mol % = 0.33% and 1.15% powders which were fired at the three temperatures of 800, 900 and 1000 °C had approximately the same grain structure, which was uniform and very porous. The grain size was about 100 nanometres, which conforms with the X-ray diffraction results, indicating that each cluster contained one or two crystallites.

The opposite was observed for Ti/(Ti+Cr) mol % = 4.42% and 6.40% powders, which were fired at 800, 900 and 1000 °C (figure 3.11). Both of these samples showed a highly agglomerated, tightly packed structure with clusters of about 5 μm in size. If the micrographs are examined closely, one may observe that the individual grains were indeed very small in size (≈100 nanometres), but that they have clustered together to form very large rocks. It was therefore considered that these powders might exhibit unusually low gas response in comparison with the earlier two sets of powders.
Figure 3.10. SEM micrographs of Ti/(Ti+Cr) mol % = 0.33% sintered at a. 800, b. 900 and c. 1000 °C and Ti/(Ti+Cr) mol % = 1.15% sintered at d. 800, e. 900 and f. 1000 °C, prepared using method two.
Figure 3.11. SEM micrographs of Ti/(Ti+Cr) mol % = 4.42% sintered at a. 800, b. 900 and c. 1000 °C and Ti/(Ti+Cr) mol % = 6.40% sintered at d. 800, e. 900 and f. 1000 °C, prepared using method two.
3.2.2.2 EFFECT OF SINTERING TIME

3.2.2.2.1 X-RAY PHOTOELECTRON STUDIES

XPS data from the second set of sensors prepared by method two showed that there was a small decrease in the amount of chromium on the surface as the firing time was increased from 15 minutes to 12 hours at 1000 °C, while the oxygen concentration (as expected) stayed constant across the series (figure 3.12).

There was a significant increase in the surface concentration of titanium with increase of firing time from 15 minutes to 1 hour, and then a smaller increase from 4 to 12 hours firing time. This was reflected directly by the Ti/(Ti+Cr) ratio on the surface with the same trend (figure 3.12). This data can be taken to mean that the solid state reaction was complete after four hours, and virtually complete after one hour at 1000 °C.

3.2.2.2.2 X-RAY DIFFRACTION STUDIES

Figure 3.13, shows a progressive sharpening of the Cr₂O₃ peak with increase of firing time at 1000 °C. In contrast to the behaviour seen when the firing temperature was increased, table 3.4 shows that there was no apparent difference between the peak positions of all the powders.
Figure 3.12. XPS surface analysis data for chromium, titanium, oxygen and Ti/(Ti+Cr) ratio for powders prepared by method two and sintered at 15 min., 1, 4 and 12 hours at 1000 °C with a target composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 
Figure 3.13. X-ray diffraction pattern of powders prepared by method two and sintered for 15 minutes, 1, 4, 12 hrs at 1000 °C and 12 hrs at 1200 °C with a target composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 
The crystallite size was determined using the Scherrer formula. Figure 3.14 shows the expected progressive increase in the crystallite size with increase of the firing time from 15 minutes to 12 hours given a constant firing temperature of 1000 °C.

<table>
<thead>
<tr>
<th>Firing temperature</th>
<th>Peak Position of Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min.</td>
<td>24.50</td>
</tr>
<tr>
<td>1 hr</td>
<td>24.51</td>
</tr>
<tr>
<td>4 hrs</td>
<td>24.48</td>
</tr>
<tr>
<td>12 hrs</td>
<td>24.50</td>
</tr>
</tbody>
</table>

Table 3.4. Peak position variation of Cr₂O₃ for different firing times at constant 1000 °C for samples prepared by method two with a target composition of Cr₁.₈Ti₀.₂O₃.

Figure 3.14. Crystallite size variation given firing time at constant temperature of 1000 °C for powders prepared by method two with a target composition of Cr₁.₈Ti₀.₂O₃.
3.2.2.23 SCANNING ELECTRON MICROSCOPY STUDIES

As can be seen from the SEM micrographs in figure 3.15 there was a gradual increase in the number of agglomerated grains as the firing time was increased from 15 minutes to 12 hours. The first sample (figure 3.15 a) had a relatively fine structure of individual grains of about 75 to 150 nanometres in size. With increase of the firing time, these individual grains agglomerated into bigger and bigger clusters (figures 3.15 b, c and d). The final sample shown (figure 3.15d) was fired at 1200 °C for 12 hours. It had a different structure, exhibiting a number of very large grains varying in size between 1 to 5 micrometers. The initial small particles had fused into each other to form these very large grains.
Figure 3.15. SEM micrographs of samples prepared by method two with a target composition of \(\text{Cr}_{1.5}\text{Ti}_{0.2}\text{O}_{3}\) and sintered for 15 minuets, 1, 4 and 12 hrs at 1000 °C & 12 hrs at 1200 °C for a, b, c, d and e respectively.
3.3 METHOD THREE

3.3.1 GENERAL

Method three was developed to overcome the mixing difficulties associated with method two. The basic co-precipitation method was still the same but surfactants were added to the mixture to help in dis-agglomeration of the small particles and a mechanical homogeniser was used to help in attaining a good mixture between the two oxides.

3.3.2 SAMPLE PREPARATION

Five powders were prepared using the co-precipitation method with the aid of surfactants. They had a target composition of $\text{Cr}_x\text{Ti}_{2-x}\text{O}_3$ ($x=1.6, 1.7, 1.75, 1.85$ and $1.9$) and were all fired at 1000 $^\circ$C for one hour. The sensors were fired in the same manner to 700 $^\circ$C for two hours after screen printing the ink.
3.3.3 ELECTRON MICROPROBE STUDIES

As can be seen from table 3.5 the measured stoichiometry varies considerably for most of the powders prepared using method three. The Ti30 sample shows significantly more titanium than the rest of the group, while both Ti25 and Ti15 have approximately the same measured composition ratio. All of the compositional variations are attributed to the preparation procedure, and as explained in chapter two the coprecipitation method has a major problem with achieving exact compositions.

<table>
<thead>
<tr>
<th>Target Code</th>
<th>Ti/(Ti+Cr) mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti40</td>
<td>7.65</td>
</tr>
<tr>
<td>Ti30</td>
<td>14.46</td>
</tr>
<tr>
<td>Ti25</td>
<td>6.34</td>
</tr>
<tr>
<td>Ti15</td>
<td>6.51</td>
</tr>
<tr>
<td>Ti10</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 3.5. Electron microprobe data for method three, showing measured composition ratio of oxide powders.
3.3.4 X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES

XPS studies were performed on all samples prepared by method three and as we can see from figure 3.16, the chromium concentration on the surface showed a slight decrease across the series. As for titanium, the opposite is true, where there is a general increase. The oxygen concentration on the surface did not vary significantly across the series. The Ti/(Ti+Cr) ratio mirrored the trend of the titanium concentration.

3.3.5 BULK VS. SURFACE COMPOSITION

Figure 3.17 shows that there was significantly more chromium in the bulk than on the surface. This big difference might be attributed to the surface contamination by carbon elements which were observed in the X-ray photoelectron studies (carbon concentration was as much as 30% on some samples). The carbon fragments probably come from the vehicle and more probably surfactants that have not been burnt off properly in the sensor-firing regime.

As for the titanium concentration, both the bulk and surface concentration were quite similar, unlike the previous two methods of powder preparation where there was significantly more titanium on the surface then in the bulk of the material. Again, this could be the effect of carbon contamination decreasing the signal.
Figure 3.16. XPS data showing chromium, titanium, oxygen and Ti/(Ti+Cr) concentration on the surface as a function of composition for samples prepared by method three.
Figure 3.17. Surface and bulk concentration for chromium, titanium and $\frac{Ti}{(Ti+Cr)}$ ratio as a function of composition for samples prepared by method three.
By using the Ti/(Ti+Cr)% ratio, we are able to cancel out the effect of surface carbon to some extent, unless the contamination layer is so thick that it adsorbs the photoelectrons. As we see from figure 3.17 the Ti/(Ti+Cr)_{surf.}/Ti(Ti+Cr)_{bulk} ratio decreased across the series.

3.3.6 X-RAY DIFFRACTION STUDIES

As can be seen from the X-ray diffraction patterns (figure 3.18), there was a single peak for Cr₂O₃ and no peak for titanium oxide. By using the Scherrer formula we can estimate the crystallite size and as table 3.6 shows there was insignificant variation in the size across the series. This is expected as all the powders were fired at the same temperature and for the same length of time.

<table>
<thead>
<tr>
<th>Composition Ti/(Ti+Cr)</th>
<th>Crystallite size / ( \mu m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.20 %</td>
<td>0.05 ± 0.05</td>
</tr>
<tr>
<td>6.34 %</td>
<td>0.05 ± 0.05</td>
</tr>
<tr>
<td>6.51 %</td>
<td>0.05 ± 0.05</td>
</tr>
<tr>
<td>7.65 %</td>
<td>0.05 ± 0.05</td>
</tr>
<tr>
<td>14.46%</td>
<td>0.05 ± 0.05</td>
</tr>
</tbody>
</table>

Table 3.6. Crystallite size variation for samples prepared by method three as a function of actual composition.
Figure 3.18: X-ray diffraction pattern of powders prepared by method three, Ti/(Ti+Cr) mol% = 1.20, 6.34, 6.51, 7.65 and 14.46.

Cr$_2$O$_3$
As for peak position of Cr$_2$O$_3$, there was a very slight decrease across the series as more titanium was present in the structure (figure 3.19). It would be extremely difficult to use the peak shift as a tool to estimate the amount of titanium present in the structure due to its small value.

Figure 3.19. Peak position of Cr$_2$O$_3$ for all powders prepared by method three as a function of actual composition.
3.3.7 SCANNING ELECTRON MICROSCOPY STUDIES

The SEM micrographs in figure 3.20 show that the samples prepared by method three showed a slight variation in microstructure. Figure 3.20 a and b show a porous and highly uniform microstructure, while figures 3.20 c, d and e show a more porous microstructure with small clusters of agglomerated particles of about 0.5 to 1 micrometer in size with similar size gaps between these clusters of particles.

The grain size was roughly the same across the series (~50 nanometres). This reflected the crystallite size estimated by the Scherrer formula from the powder diffraction pattern.
Figure 3.20. SEM micrographs of powders prepared by method three, Ti/(Ti+Cr) mol% = a) 7.65, b) 14.46, c) 6.34, d) 6.51 and e) 1.20%.
3.4 COMPARISON BETWEEN METHODS

3.4.1 GENERAL

Although all three methods of powder preparation should result in chromium titanium oxide with different microstructure but similar stoichiometries, the results show differently. The last part of this chapter compares these three preparations in bulk and surface compositions, with the powder diffraction results and finally by their microstructure.

3.4.2 X-RAY PHOTOELECTRON STUDIES

XPS studies (figure 3.21) show that there is a gradual increase in titanium concentration on the surface as the composition ratio Ti/(Ti+Cr)% increases across the three methods. As was explained earlier on in this chapter, method two showed an increase in the amount of titanium on the surface as the firing temperature was increased from 800 to 1000 °C. This signifies that more titanium is segregating out onto the surface of the oxide as the firing temperature is increased. By comparing the powder that was sintered at 1000 °C and prepared by method two with that of methods one and three we see that there is little difference between them within experimental error. There was one sample which exhibited an unusually high titanium concentration, that was prepared by method two and fired at 1000 °C and had a calculated composition of Ti/(Ti+Cr)% = 1.15 and a theoretical composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. The trend for the Ti/(Ti+Cr)% on the surface is very similar to that of titanium.
As for the chromium, the trend was opposite that of titanium (figure 3.21), where there is a decrease in the chromium concentration as the Ti/(Ti+Cr)\% ratio increased. If we look at method two first, again we see a gradual decrease in chromium concentration as we increase the firing temperature from 800 to 1000 °C. And if we compare the sample that was fired at 1000 °C and prepared by method two with that of method one and three we see a small difference between the chromium concentration trend across the series.

There is very little variation in oxygen concentration in any of the three methods when looked at independently. But if we compare the three methods together we see that methods one and three are very similar while method two has a higher oxygen concentration. This could be attributed to carbon contamination on the surface which was discussed earlier in the chapter.
Figure 3.21. XPS data showing titanium, chromium, oxygen and Ti/(Ti+Cr)% ratio on the surface for powders prepared by methods one, two and three as a function of bulk composition.
3.4.3 X-RAY DIFFRACTION STUDIES

The information extracted from the X-ray diffraction patterns can be split into two parts. First, the crystallite size obtained from the Scherrer formula, and as we see from figure 3.22 that method one shows the highest crystallite size of about \( \sim 0.12 \, \mu m \). While the second method produced a crystal size significantly smaller (\( \sim 0.07-0.09 \, \mu m \)) and this is obviously due to the preparation procedure used. By far the smallest crystallite size was that for powders produced by method three (\( \sim 0.05 \, \mu m \)). The reduction in crystal size attributed to the use of surfactants which help in dis-agglomeration of crystals.

The second part is the Cr\(_2\)O\(_3\) peak position, and as we see from figure 3.23 there is insignificant peak shift between the samples. The peak shift is most obviously observed in unreacted samples i.e. where powders have been fired at low temperatures and have not formed a solid solution between the two oxides (figure 3.8). But as the oxides form a solid solution the peak shift becomes insignificant. Figure 3.23 also shows that the amount of titanium oxide present has very small effect on the peak position.
Figure 3.22. Crystallite size of powders prepared by methods one, two and three as a function of bulk composition.

Figure 3.23. Cr$_2$O$_3$ peak position of powders prepared by methods one, two and three as a function of bulk composition.
3.4.4 SCANNING ELECTRON MICROSCOPY STUDIES

SEM micrographs complement X-ray diffraction data, for instance the crystallite size estimated from XRD patterns is usually confirmed in the SEM micrographs as long as the powder has not been fired for long periods of time. This means that if the powder has been fired for a short period (~1 hour) we can see individual crystallites or small clusters of several crystallites formed together (figure 3.4). But if the powder is fired for longer (12 hours) and at higher temperature (1200 °C) we will lose these clusters and observe very large grains (~1-5 μm) forming (figure 3.15e). The crystallite size also increases according to XRD data (figure 3.14) but these crystallites are not observed in the SEM micrographs when the powders are fired for long periods of time due to their fusing together to form the very large grains.

Methods two (figures 3.10, 3.11 and 3.15) and three (figure 3.20) produced very similar powders and grain structures. This is expected as both methods use the same preparation technique, the only exceptions being figure 3.11 and 3.20c&d. We should expect progressive grain growth and a change in the microstructure when we fire the powders for longer periods of time, and this is what we observe in figure 3.15. Method one also produced a highly uniform powder, but with a slightly larger crystallite size (figure 3.4). It would appear that the use of surfactants in method three was effective in preventing agglomeration.
3.5 EFFECT OF SUBSTRATE FIRING TEMPERATURE ON RESPONSE

3.5.1 GENERAL

In this section we are going to discuss the effects of the gold electrode interaction with the oxide material printed on it, and the effects of that on the response to certain test gases. We are going to discuss the effect of bonding agents added to the gold when it was printed on to the alumina substrate and the possibility of these fluxes migrating to the oxide layer once the sensor has been fired, and also the effect of the firing temperature of the sensor on response.

There are low concentrations of certain bonding agents that are added to the gold during manufacturing before it is printed on to the alumina substrate, and small amounts of these fluxes will migrate to the oxide layer once it is fired (at the final stage of the sensor preparation, after the oxide layer is printed and the whole sensor is fired in order to ‘cake’ the powder on the substrate).\(^{62-66}\)

Therefore, we set up an experiment where a batch of powder was prepared using preparation method one which had a theoretical composition of \(\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3\) and fired at 1000 \(^{0}\)C for one hour. This powder was then printed in the normal way on to the alumina substrate (chapter two). The sensors were subsequently fired at four temperatures of 750, 800, 850 and 900 \(^{0}\)C to observe the differences (if any) on the response of the sensors.
There are no compositional or microstructure variations between these powders as they are all prepared and fired in the same manner, the only difference between them is the subsequent firing temperature of the substrate. Therefore the variation in response will solely be due to this factor.

3.5.2 GAS RIG RESULTS

As we can see from figure 3.24 (experiments operated at 350 °C), there is no effect of substrate firing temperature on the response to carbon monoxide, but we still see the reverse sensitivity gradient (chapter four). As for ethanol, there is a significant increase in response as the substrate firing temperature is increased from 750 to 900 °C. This increase is only observed on the small and medium electrodes with no effect on the large electrode, this might be due to the fact that only the small and medium electrodes are laser scribed and not the large electrode (large electrode is screen printed).

The other gas for which we see an effect is ammonia, where the response decreases as the substrate firing temperature is increased, but this time the effect is apparent on all the small, medium and large electrodes. The other unusual observation is that we see a reverse concentration gradient, and this concentration gradient decreases as the substrate firing temperature is increased. The final gas tested is relative humidity, here again we see an unusual reverse concentration gradient, but this time the response on the medium electrode is slightly larger than that of the small electrode.
The carbon monoxide trend does not change once the operating temperature is increased to 400 °C (figure 3.25), but we see a decrease in response on all devices.

Ethanol on the other hand shows a complete transformation when the experiment is operated at 400 °C, where we see the response on the small, medium and large electrodes virtually identical with no apparent concentration gradient for each firing temperature. But we still see an increase in response as the substrate firing temperature is increased from 750 to 900 °C. Therefore what we are observing here is that the response on the large electrode shifts from being constant and the firing temperature having no effect on it (at 350 °C) to increasing with substrate firing temperature (at 400 °C). The final two test gases ammonia and relative humidity both show no variation in response with increase in substrate firing temperature and no concentration gradient.

There are obviously significant variations in response that are affected by the substrate firing temperature, and these variations are not linked to composition or the microstructure of the oxide material as these are both constant in this experiment. But what these variations are linked to is the interaction of the gold electrodes with the oxide, and it is expected there are two possibilities here; first the possibility of fluxes migrating from the bonding agents that are used when the gold electrodes are applied on to the substrate and / or the interaction of alumina and the possibility of $\text{Al}_2\text{O}_3$ affecting the oxide material and hence the response.

To see if either one or both of these factors affect the response two experiments were devised; first is sectioning of two sensors, one where the substrate is fired at 700 °C and the other at 900 °C at the small electrode gap (20 μm wide) and perform electron microprobe analysis maps on that region to see what other elements are present near the gold electrode.
boundaries with the oxide material, and to compare the concentrations of those elements between the two devices. The second experiment is to substitute \( \text{Cr}_2\text{O}_3 \) with \( \text{Al}_2\text{O}_3 \) and see what affect that has on the response (chapter four).
Figure 3.24. Response of sensors whose substrates were fired at 750, 800, 850 and 900 °C to different test gases at 350 °C operating temperature for samples prepared by method one with a theoretical composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$. 
Figure 3.25. Response of sensors whose substrates were fired at 750, 800, 850 and 900 °C to different test gases at 400 °C operating temperature for samples prepared by method one with a theoretical composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 
3.5.3 CONCENTRATION GRADIENT

RESULTS

As can be seen from figure 3.26 (gradient at 350 °C operating temperature), there is a reverse sensitivity gradient for carbon monoxide and this increases slightly with increase in substrate firing temperature. Ethanol shows an even more significant increase in concentration gradient as the substrate firing temperature is increased from 750 to 900 °C. This affect changes from being a small concentration gradient at 750 °C to no concentration gradient at 800 °C and finally a reverse concentration gradient at 850 and 900 °C substrate firing temperature. Ammonia and relative humidity both show a reverse concentration gradient with little affect of substrate firing temperature on the gradient.

As for sensors operated at 400 °C (figure 3.27), we see similar trends as before for carbon monoxide and ammonia. Ethanol and relative humidity on the other hand show no concentration gradients when operated at this higher temperature.
Figure 3.26. Concentration gradient for devices fired at 750, 800, 850 and 900 °C and operated at 350 °C for samples prepared by method one with a theoretical composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 
Figure 3.27. Concentration gradient for devices fired at 750, 800, 850 and 900 °C and operated at 400 °C for samples prepared by method one with a theoretical composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 
3.5.4 ELECTRON MICROPROBE STUDIES

Electron microprobe studies were performed on two devices that were sectioned through the small electrode gap (~20 μm wide) and polished progressively down to 0.25 μm using diamond paste. The substrates of the two devices were fired at 700 and 900 °C; these were carefully chosen in order to see the differences between them and whether the firing temperature has any affect on the elements migrating to the oxide material and hence affecting the response.

Ten elements were chosen for analysis, some were chosen on the basis that they were used as bonding agents in the gold electrodes (Cd, Cu, Mg and Fe), some were thought could form salts (Si and Ca) and some to confirm their presence (Al, Au, Cr and Ti).

As we can see from figure 3.28, there is significantly more cadmium and copper migrating from the two gold electrodes to the oxide layer in the device that was fired at 900 °C then that found in the device that was fired at 700 °C (figures 3.28 a & b). Once these elements migrate out towards the oxide layer, they will probably react with it at these high temperatures to form other species, which will affect the response of the sensors. This result is highly significant and is probably one of the main reasons why we are observing some of the unexpected results seen earlier in the chapter. Calcium also migrates outwards, but at a significantly reduced rate than that of cadmium or copper at both firing temperatures (figure 3.28 c). Magnesium, iron and silicon showed no effect near the electrodes, and are thought to have no affect on the response (figure 3.29 a, b & c).
Figure 3.28. Electron microprobe data showing two sectioned sensors fired at 700 and 900 °C for a) cadmium, b) copper and c) calcium elements, for samples prepared by method one with a theoretical composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 
Figure 3.29. Electron microprobe data showing two sectioned sensors fired at 700 and 900 °C for a) magnesium, b) iron and c) silicon elements, for samples prepared by method one with a theoretical composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 
As for chromium (figures 3.30 a), it showed as expected an extremely high count for both devices. Titanium on the other hand showed a number of unreacted titanium oxide particles probably about 1-2 micrometers in size (represented by red spots on the microprobe map, figure 3.30 b). This is expected, especially as the samples were prepared using method one, where commercial titanium oxide was used and not the one prepared through the colloidal method. This, again, confirms what was explained in chapter two about the reason why it is necessary to use ultra fine particles of titanium oxide and not the commercial product, which has a larger size particle.

Aluminium and gold (figures 3.31 a & b respectively), both show as expected high counts for their respective areas with no deviation or migration into other areas of the material.
Figure 3.30. Electron microprobe data showing two sectioned sensors fired at 700 and 900 °C for a) chromium and b) titanium elements, for samples prepared by method one with a theoretical composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 
Figure 3.31. Electron microprobe data showing two sectioned sensors fired at 700 and 900 °C for a) aluminium and b) gold elements, for samples prepared by method one with a theoretical composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 


3.6 SURFACE CATALYSED COMBUSTION

3.6.1 GENERAL

In section 1.4 the idea was introduced that sensor response was modified by the concentration gradient caused by surface catalysed combustion of the gas. The thrust of this thesis is to use multiple electrode devices to probe this concentration gradient and thereby separate out the affects of microstructure on this gradient from the affects of microstructure on other aspects of sensor behaviour.

Williams and Pratt\textsuperscript{33} developed a simple model for multiple electrode devices, in which the porous sensor layer was treated as a homogenous medium. The device response was characterised by two dimensionless parameters: $K_p$, the gas sensitivity, and $K_T = kh^2/D'$, which characterised the concentration gradient caused by the surface catalysed combustion. Here the $k$ denotes the pseudo first order rate constant for the reaction, $h$ denotes the layer thickness and $D'$ denotes the gas diffusivity within the porous sensing layer. The parameter $D'$ is dependent on the microstructure and $k$ upon the internal surface area. The objective of the work described in this section was to estimate the rate constant and obtain its temperature dependence. This is essential background to understanding the response behaviour of the materials.
3.6.2 THEORY

A flow-through, packed bed reactor was used; the decrease in concentration, $c$, of the target gas from the initial value $c_0$ when the gas mixture flowed at known volume flow rate $v$, through a bed of powder of known weight, $m$, depth, $h$, cross section area, $A$, and furnace at temperature, $T$, and the final concentration at the exit of the bed $C_f$ were measured.\(^{33}\)

The time the gas spends in the bed is:

$$t = \frac{hA\varepsilon}{v} \quad \ldots 1$$

And the combustion rate law is expressed as a pseudo-first-order process, where the rate constant is some function $k(c, T)$ of the reactant gas concentration and the temperature:

$$\frac{dc_f}{dt} = - k(c_f, T)c_f \quad \ldots 2$$

$\varepsilon$ denotes the volume fraction of gas in bed:

$$\varepsilon = 1-\left(\frac{m}{Ah\rho}\right) \quad \ldots 3$$

Where $\rho$ is the density. From equations 1 and 2, $\Delta c = c_0 - c_f$,

$$\frac{d(\Delta c)}{d(h/v)} = - k(c_f, T) c_f A\varepsilon \quad \ldots 4$$

If the reaction is first order, the equations are integrated and the result in terms of conversion, $\gamma = (1 - c_f/c_0)$ is:

$$\ln(1-\gamma) = -(A\varepsilon h/v)k(T) \quad \ldots 5$$

$$\ln(1-\gamma) = \text{const. } k(T) \quad \ldots 6$$
3.6.3 EXPERIMENTAL

3.6.3.1 APPARATUS

Two powders with a theoretical composition of \( \text{Cr}_{1.8} \text{Ti}_{0.2} \text{O}_3 \) were prepared using method four, one was sintered at 1000 °C for one hour and the other was fired at 1200 °C for twelve hours. An apparatus was set up as shown in figure 3.22, which consisted of a glass tube with a frit, which held the 500 mg of chromium titanium oxide material (unless otherwise stated). The tube was inserted into a computer controlled furnace. The gas outlet was connected up to a detector.

3.6.3.2 EXPERIMENT DESIGN

Three types of experiments were performed: (a) a slow temperature ramp (1 °C/min.) with gas stream alternately switched between air and air containing target gas with 15 minutes in each state. (b) a temperature ramp at (5 °C/min.) with the gas stream being simply air plus target gas, unswitched. (c) a temperature programmed desorption experiment, flowing gas at known concentration for known time over powder held at room temperature, switching the gas stream to air and then commencing the temperature ramp.

3.6.3.3 DETECTOR CALIBRATION

A commercial gas sensor of nominal composition of \( \text{Cr}_{1.8} \text{Ti}_{0.2} \text{O}_3 \), supplied by Capteur Sensors** and operated at 400 °C was used as a detector. It was calibrated in flowing gas stream of known concentration. Figure 3.33 shows the calibration graph.

** Supplier, Capteur Sensors, 11 Moorbrook Park, Didcot, OX11 7HP.
Figure 3.32. Surface catalysed combustion experiment.
Figure 3.33. Calibration curve of commercial gas sensor for carbon monoxide, acetone, ethanol and ammonia.
3.6.4 RESULTS AND DISCUSSION

3.6.4.1 SWITCHED GAS EXPERIMENT

The switched gas experiment was only performed on the powder that was fired at 1000 °C for one hour. The three test gases used were carbon monoxide, acetone and ammonia.

3.6.4.1.1 CARBON MONOXIDE COMBUSTION

As can be seen from figure 3.34 the behaviour with this gas was exactly as expected for this type of experiment. There was a clean switch in the detector response corresponding to the switch in gas atmosphere. The combustion commenced at about 300 °C. Since the combustion product, carbon dioxide, is known to give no response at low concentrations in air on the detector, the calibration graph of figure 3.33 could be used to calculate the concentration of carbon monoxide in the exit stream.

Using equation 6 the rate constant for the surface catalysed combustion was obtained as a function of temperature and is shown in figure 3.35. Figure 3.35 reveals as expected that the rate constant increases as the furnace temperature is increased and the carbon monoxide gas combusts on the surface of the chromium titanium oxide, this gives an activation energy of 16 kJmol⁻¹.
Figure 3.34. Switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with carbon monoxide as test gas.

Figure 3.35. Rate constant for switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with carbon monoxide as a test gas.
CHAPTER THREE

3.6.4.1.2 ACETONE COMBUSTION

This gas did not show clearly distinguishable steps in detector signal when the gas was switched (figure 3.36). Furthermore, at the start of the experiment, when both gas flow and temperature ramp were commenced the detector signal was zero. The detector signal rose with increasing temperature and then fell again to zero.

The behaviour is characteristic of a system in which the gas is strongly adsorbed onto the material of the bed. The initial delay before gas is detected in the exit stream should be dependent on the surface area. The rise in signal with increasing temperature is due to desorption of the gas from the surface. The subsequent fall is due to the surface catalysed combustion. From this last section of the curve, values of the rate constant for the surface catalysed combustion were obtained by application of equation 6 as shown in figure 3.37.

Figure 3.36. Switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with acetone as test gas.
Figure 3.37. Rate constant for switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with acetone as a test gas.
3.6.4.1.3 AMMONIA COMBUSTION

Ammonia behaved as a strongly adsorbed gas and showed the same general features as acetone. However, following the onset of the surface catalysed combustion the detector signal decreased below the resistance value found in clean air (figure 3.38).

The result is consistent with a reaction product which causes a resistance decrease on the sensor, and with strong adsorption, probably of the reaction product as well as ammonia. Sensors of this type give a resistance decrease in oxidising gases, so it is likely that the reaction product is NO, NO₂.

Because of the effect of the reaction product, the calibration cannot be used to derive the ammonia concentration. However, the onset temperature for the surface catalysed combustion was at about 160 °C, and the reaction appeared complete at about 300 °C.

![Figure 3.38. Switched gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with ammonia as test gas.](image)
3.6.4.2 CONSTANT GAS EXPERIMENT

Two test powders were used in the constant gas experiment, the first was fired at 1000 °C for one hour and the second was fired at 1200 °C for twelve hours. Three different test gases were used, carbon monoxide, acetone and ethanol.

3.6.4.2.1 CARBON MONOXIDE COMBUSTION

Figure 3.39 shows that for the powder that was fired at 1000 °C for one hour, there was no combustion of carbon monoxide until the furnace temperature reached 386 °C (point 1), the combustion rate increased as the furnace temperature increased to the maximum (500 °C, point 2). The sensor calibration curve (figure 3.33) gave the gas concentration in the exit stream as 500 ppm, 50% of the inlet concentration. The second powder, that was fired at 1200 °C for 12 hours, showed (figure 3.40) no combustion at any temperature up to and including 500 °C. This is expected and is attributed to the low surface area of the powder due to the high firing temperature and the prolonged periods of firing time which leads to a much larger grain size. Surface area measurements revealed that the sample that was fired at 1000 °C for one hour had a surface area of 5.85 m² / g significantly higher than the other powder which had a very low surface area. It is evident from figure 3.35 that a decrease in rate constant by such a factor could result in an undetectably small degree of reaction.
Figure 3.39. Constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with carbon monoxide as test gas.

Figure 3.40. Constant gas experiment for powder prepared by method four and sintered at 1200 °C for 12 hour with carbon monoxide as test gas.
Figure 3.41. Rate constant for constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour and 1200 °C for 12 hours with carbon monoxide as a test gas.
3.6.4.2.2 ACETONE COMBUSTION

Figure 3.42 shows a gradual increase in detector response to point 1, which indicates that it takes about 10 minutes to saturate the 500 mg bed of powder (fired at 1000 °C for 1 hour). A sharp decrease in response is then observed until point 2 (211 °C furnace temperature) which suggests that the acetone starts to combust on the surface of the oxide at 126 °C and is fully combusted by 211 °C (point 2). Point 2, coincidentally, is lower than the original base line, which means that the acetone combustion product gives a slight negative response to a p-type semiconductor. The response of the sensor increases slightly as the temperature is increased further towards point 3 where it reaches 296 °C, then it falls back slightly as the furnace temperature is increased (346 °C) towards point 4.

As for the powder that was fired at 1200 °C for 12 hours (figure 3.43), a different behaviour is observed, where we see a sharp increase in detector response to acetone (point 1), which means there is no acetone absorption on the oxide as in the sample in figure 3.42. A slow decline in response is then observed as the furnace temperature reaches 311 °C (point 2), this point represents about 7.5 ppm of acetone (10 ppm acetone supply). There is a sharp increase in the combustion rate as we go from point 2 to point 3 (500 °C furnace temperature) where the base line goes back to its original state. These results are confirmed by the rate constant calculation (figure 3.44), where we see the acetone combustion at a much lower temperature for the powder that was fired at 1000 °C for one hour compared to the powder that was fired at 1200 °C for twelve hours. The activation energy for combustion on the 1000 °C powder was higher (124 kJmol⁻¹) than on the 1200 °C powder (15 kJmol⁻¹).
Figure 3.42. Constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with acetone as test gas.

Figure 3.43. Constant gas experiment for powder prepared by method four and sintered at 1200 °C for 12 hour with acetone as test gas.
Figure 3.44. Rate constant for constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour and 1200 °C for 12 hours with acetone as a test gas.
3.6.4.2.3 ETHANOL COMBUSTION

Ethanol the third test gas (figure 3.45) shows a very similar trend to that of acetone, where the response of the sensor shows a slow increase to point 1 which represents 136 °C furnace temperature and about 5 ppm of ethanol (50% of original supply) for the first powder (fired at 1000 °C for 1 hour). Then all the ethanol that has adsorbed on to the oxide will start to combust as the temperature is increased to 191 °C point 2. This point is slightly below the original base line, but as the temperature is increased to 301 °C point 3 we see a base line recovery, the base line drops slightly again as the temperature is increased to 326 °C (point 4) where it is maintained.

As for the powder that was fired at 1200 °C for 12 hours, the sensor shows a sharp response towards ethanol with no combustion until point 1 is reached which represents 216 °C furnace temperature (figure 3.46). The ethanol starts to combust as we go from point 1 to point 2 (436 °C furnace temperature) where the ethanol was fully combusted. Both these results are confirmed by the rate constant calculation, where ethanol combusts at a lower temperature on the powder that was fired at 1000 °C for one hour relative to the powder that was fired at 1200 °C for twelve hours (figure 3.47). The activation energy for combustion on the 1000 °C powder was higher (105 kJmol⁻¹) than on the 1200 °C powder (52 kJmol⁻¹).
Figure 3.45. Constant gas experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with ethanol as test gas.

Figure 3.46. Constant gas experiment for powder prepared by method four and sintered at 1200 °C for 12 hour with ethanol as test gas.
Figure 3.47. Rate constant for constant gas experiment for powder prepared by method four and sintered at 1000°C for 1 hour and 1200°C for 12 hours with ethanol as a test gas.
3.6.4.3 TEMPERATURE PROGRAMMED DESORPTION EXPERIMENT

This experiment was carried out using ammonia only. The objective was to compare the different materials with respect to their adsorption capacity for ammonia and for the reaction product.

Following adsorption of ammonia at room temperature on to the powder that was fired at 1000 °C for one hour, ammonia showed a sharp response when the gas was switched back to air and the ramp commenced (point 1, 41 °C furnace temperature, figure 3.48). The desorption of ammonia started at point 1 and was not complete when point 2 was reached (316 °C, furnace temperature). Point 2 is below the original baseline which means that the adsorbed ammonia on the 100 milligram bed was still present even until the end of the 6 hour experiment at 500 °C furnace temperature, because it is probably the combustion product that is causing the base line to go slightly below its original position. As for the second powder (1200 °C, 12 hours), a smaller amount of ammonia was adsorbed on the surface and hence there was a smaller response on the detector (figure 3.49). The effects on the 1200 °C powder were smaller, consistent with the smaller surface area. Again, desorption of ammonia required a temperature of at least 500 °C.
Figure 3.48. Combustion experiment for powder prepared by method four and sintered at 1000 °C for 1 hour with ammonia as a test gas.

Figure 3.49. Combustion experiment for powder prepared by method four and sintered at 1200 °C for 12 hours with ammonia as a test gas.
CHAPTER FOUR

GAS RESPONSE OF
CHROMIUM TITANIUM OXIDE
CHAPTER FOUR

GAS RESPONSE OF CHROMIUM TITANIUM OXIDE

4.1 GENERAL

This chapter first discusses separately the gas response of sensors prepared by each method and then the final part makes a comparison between the responses obtained with all the different preparation methods.

Sensors were tested towards five gases: 10 ppm acetone, 10 ppm ethanol, 100 ppm ammonia, 1000 ppm carbon monoxide and 95% relative humidity in dry laboratory air. All sensors were tested at 350 °C operating temperature; some were further tested at 400 and 450 °C.

Most of the devices tested were printed on a multiple electrode substrate and hence three separate signals are obtained from the small, medium and large electrodes. The response of the sensors was compared by looking at the response on the small gap electrode of the devices in question. The relative responses observed for the different electrode gaps were used to assess the gradients of response through the devices. In all the following, response is defined as the ratio R/R₀, where R denotes resistance in gas and R₀ in clean, dry air.
4.2 METHOD ONE

All four sensors tested were prepared in the same manner and fired at the same temperature and for the same length of time. There seemed to be insignificant variation in microstructure (figure 3.5) between the four sensors hence the variation in response should be primarily due to difference in composition. However, as will be seen later, judgement of microstructure based on the surface view could be misleading.

A typical example of an experiment is shown in figure 4.1, where it shows the raw data for the response to carbon monoxide (resistance as a function of time) on the small, medium and large electrodes where the sensors were operated at 350 °C for all four sensors. Figure 4.2 illustrates a typical example of response law fit, where the resistance is plotted as a function of carbon monoxide gas concentration for both actual and fitted data.

The fit is to a function of the form \( \frac{R}{R_0} = (1+kc)^\beta \). The values of \( \beta \) (figure 4.3) are smaller than expected: a value of \( \beta = 0.5 \) is anticipated from the literature. In effect, for the data shown in figure 4.2, the response rises sharply for gas concentrations up to 125 ppm and then varies little for further increase of gas concentration. For all the gases studied except water vapour, the values of \( \beta \) were the same for all three electrode pairs and increased systematically with increase of titanium content. However, for water vapour, values of \( \beta \) are highly variable both between devices and between electrodes. Most typically, however, \( \beta \) lay in the range of 0.5 – 1.
Figure 4.4 shows the variation in response between the sensors when the sensor composition, operating temperature and the test gas are varied. A large increase in response to all gases with decrease of the operating temperature from 450 to 350 °C is observed. A small increase of response with increasing titanium content across the series is evident for all test gases. This variation is more apparent as the operating temperature is decreased to 350 °C.

The behaviour of the gradient of response through the devices, measured by the ratio of response on small/large spacing, seems unexpected in some respects (figure 4.5). Water vapour shows no variation in response ratio with composition and operating temperature, and the response ratio is close to unity. This is expected behaviour when there is neither a gradient of sensitivity nor of gas composition through the thickness of the sensor layer.

Unusually, acetone, for which a large gradient of gas concentration through the layer is expected, shows behaviour almost identical to water vapour. Ammonia shows no influence of a concentration gradient, despite the fact that this gas, also, reacts rapidly on the sensor surface (see section 3.6.1).

Carbon monoxide, however, which is also unreactive on the sensor surface shows a signal which is significantly larger on the small electrode spacing than on the large, the effect increasing with increasing titanium content of the material.
Figure 4.1. Raw data for typical experiment, resistance as a function of time and CO gas concentration, for sensors prepared by method one. Test gas carbon monoxide with concentration of 1000, 500, 250, 125 ppm for each of the four steps, sensors operated at 350 °C.
Figure 4.2. Typical response law fit, resistance as a function of gas concentration, for sensors prepared by method one. Test gas carbon monoxide with concentration of 1000, 500, 250, 125 ppm, sensors operated at 350 °C.
Figure 4.3. Values of $\beta$ for all sensors prepared using method one as a function of composition.
Figure 4.4. Response of all sensors prepared using method one as a function of composition.
Figure 4.5. Response gradient of sensors prepared using method one as a function of composition.
4.3 METHOD TWO

4.3.1 RESPONSE VARIATION WITH SENSOR COMPOSITION & SINTERING TEMPERATURE

In this section, response data for material prepared with fixed firing time of one hour but different firing temperatures is presented. All materials were fired onto the substrate at 700 °C for 2 hours. Figure 4.6 shows a typical experiment for three sensors with a composition of Ti/(Ti+Cr)=6.40% and firing temperatures of 800, 900 and 1000 °C for carbon monoxide as a test gas at 350 °C operating temperature. Figure 4.7 shows the resistance as a function of carbon monoxide gas concentration for the same experiment. As for method one, the resistance rose markedly in response to a low gas concentration and then varied little more. The response order, β was low, β ~ 0.1 (figure 4.8), and independent of electrode spacing.

The base line resistance increased markedly with increase of firing temperature from 800 to 900 °C. All sensors that were fired at 800 and 900 °C showed a low response to all gases (figure 4.8). There was a general increase in response as the powder firing temperature increased and the response also increased slightly as the titanium content increased across the series. The response to carbon monoxide was significantly higher than that the other gases. Over the range of compositions explored, there seemed a higher sensitivity to all the gases for the particular composition of Ti/(Ti+Cr)=1.15%; this device had the higher value of β (~0.2) and was the only one with sensitivity comparable with that shown by method one.
The behaviour of the response gradient was similar to that observed for method one: no gradient for ammonia or acetone, and an inverse gradient for carbon monoxide, this latter showing a slight increase with increasing titanium content. Ethanol also showed no apparent gradient, and this was also an unexpected result (figure 4.9).
Figure 4.6. Raw data for typical experiment, resistance as a function of time, for sensors prepared by method two and sintered at 800, 900 and 1000 °C. Test gas carbon monoxide with concentration of 1000, 500, 250, 125 ppm, sensors operated at 350 °C.
Figure 4.7. Raw data for typical experiment, resistance as a function of gas concentration, for sensors prepared by method two and sintered at 800, 900 and 1000 °C. Test gas carbon monoxide with concentration of 1000, 500, 250, 125 ppm, sensors operated at 350 °C.
Figure 4.8. Values of $\beta$ for all sensors prepared using method two as a function of composition.
Figure 4.9. Response of all sensors prepared by method two and sintered at 800, 900 and 1000 °C as a function of composition.
Figure 4.10. Concentration gradient of all sensors prepared by method two and sintered at 800, 900 and 1000 °C as a function of composition.
4.3.2 RESPONSE VARIATION WITH POWDER SINTERING TIME AND TEMPERATURE

All the powders in this set of sensors had the same target composition of $\text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3$, so the differences in response should be attributable to variation in microstructure due to different powder firing regimes. All powders were printed on substrates with just one electrode gap so response gradient information for these sensors was not available. The powders were all fired onto the substrate at 700 °C for two hours.

Figure 4.11 shows the variation in response with firing time and temperature. The trend for the response for the three different gases tested was very similar. First for materials sintered at 1000 °C there was a slight decrease in response as the firing time was increased from 15 minutes to one hour and then four hours. There was little further change in response when the firing time was increased to 12 hours. The effect was much more marked on the response to carbon monoxide and acetone than on the response to ammonia. The response decreased significantly with increase of the firing temperature from 1000 to 1200 °C. Figure 3.15 showed the changes in microstructure which followed from different regimes. In particular, there was a major change in the microstructure with increase of firing temperature from 1000 to 1200 °C (figure 3.15e); 12 hours at 1200 °C caused the average grain size to increase to between one and five micrometers.
Figure 4.11. Response for powders prepared by method two and sintered at 1000 and 1200 °C as a function of sintering time.
4.4 METHOD THREE

Again, this method resulted in devices with very small response order $\beta < 0.1$, except for the response to water vapour, for which $\beta$ was independent of the electrode gap and varied in no systematic fashion between 0.5 and 1 (figure 4.12). Two of the devices also showed, in response to acetone, values of $\beta$ increase with electrode gap and lying in the range of 0.25 and 0.4.

Figure 4.13 shows no trend of response with composition for ammonia, ethanol, carbon monoxide and relative humidity, but does show increase response (correlating with increased response order) to acetone with increasing titanium content. The variability in response about the trend was, however, greater than that found for the other methods. This variability was particularly marked for the response to acetone, ethanol and water vapour, and could be interpreted as the response for the two compositions marked A & B being higher than expected, or as those for compositions C & D being lower than expected.

Except for carbon monoxide, which showed the same inverse response gradient as all the other preparations, all the gases showed no response gradient, again as found before. However, there seemed more variability, and it seemed that compositions A & B were in some way different to the others (figure 4.14). Composition A & B were those with the larger $\beta$ in response to acetone, they showed an ‘inverse gradient’ of response to acetone, which is completely unexpected.
Figure 4.12. Values of $\beta$ for all sensors prepared using method three as a function of composition.
Figure 4.13. Response of all sensors prepared by method three as a function of composition.
Figure 4.14. Concentration gradient of all sensors prepared by method three as a function of composition.
4.5 METHOD FOUR

All powders prepared by method four had the same target composition of \( \text{Cr}_{1.8}\text{Ti}_{0.2}\text{O}_3 \), hence the variation in response should be attributed to microstructure effects. The powders prepared from this batch were fired at three temperatures of 1000 (for 1, 12 and 72 hrs), 1100 (for 1 and 4 hrs) and 1200 °C (for 1, 4 and 12 hrs).

Powders prepared by this method were pressed into pellets, hence the size of the response will be different to all the other previous results obtained from methods one, two and three. But what we are looking for in this experiment is the trend that these powders produce due to the fact they are fired at different temperatures and for different lengths of time. Effects due to interaction with the electrodes and substrate should also be absent. All pellets were pressed at 1 ton into 13 millimetre diameter pellets. The thickness of the pellets was not measured but was approximately 2 mm. The gas concentration dependence was also not measured.

Figure 4.15 shows that the response at 350 °C operating temperature to changes of relative humidity tended to decrease as the firing temperature increased from 1000, 1100 to 1200 °C, and also to decrease with increase of the firing time for each individual firing temperature. The effects were most marked for the longest firing time and the highest firing temperature.

The opposite trend was observed for the response to carbon monoxide (figure 4.15), where the response was increasing as the firing temperature and time was increased throughout the series, again with the effects most marked for the highest temperature and longest firing time.
A similar trend was observed at 400 °C operating temperature (figure 4.16), but with a slightly lower response for all gases tested. The effect of water vapour on the response to carbon monoxide appeared to be unchanged by the change of the firing conditions in the range investigated.
Figure 4.15. Response to CO, wet CO and relative humidity for all powders prepared by method four at 350 °C operating temperature, target composition of Cr₁.₅Ti₀.₂O₃.
Figure 4.16. Response to CO, wet CO and relative humidity for all powders prepared by method four at 400 °C operating temperature, target composition of Cr_{1.5}Ti_{0.2}O_3.
4.5.1 EFFECT OF PELLET SINTERING ON RESPONSE

What we have shown until now is the effect of firing temperature and time in the powder preparation on the response to certain gases to powders prepared by method four. For the next experiment, the powders were fired again after pressing the pellet using the same regime (time and temperature) as that for the initial firing. The temperature and time for the two stages were respectively 1000, 1100 and 1200 °C and one hour. The idea was to see the effect of growing the necks between the grains on the response of these materials.

Figure 4.17 shows that there was little or no effect of the additional firing of the pellet, other than the effects indicated in figure 4.16, where it was shown that increasing the firing time from one to four hours may have caused a slight increase of response to gas and increasing firing temperature caused a decrease in response to water vapour. The same results are observed for devices operated at 350 °C (figure 4.18) with the exception that they all showed a higher response than the devices that were operated at 400 °C.
Figure 4.17. Response for various devices prepared by method four and operated at 400 °C, target composition of Cr_{1.8}Ti_{0.2}O_3.

Figure 4.18. Response for various devices prepared by method four and operated at 350 °C, target composition of Cr_{1.8}Ti_{0.2}O_3.
4.5.2 EFFECT OF SINTERING TIME & TEMPERATURE ON BASELINE RESISTANCE

Figure 4.19 & 4.20 show that there was a significant variation in resistance in air with change in firing time and temperature. The baseline resistance increased as the firing temperature and time increased. The pellet thickness was not measured nor was the apparent density of the pellet.

Figure 4.19. Effect of baseline resistance on devices prepared by method four and operated at 400 °C, target composition of Cr$_{1.8}$Ti$_{0.2}$O$_3$. 

187
Figure 4.20. Effect of baseline resistance on devices prepared by method four and operated at 350 °C, target composition of Cr1.8Ti0.2O3.
4.6 RESPONSE COMPARISON BETWEEN METHODS 1, 2 & 3

Various gas experiments have been performed on devices and at various operating temperatures for powders that have been fired at different temperatures. What is to be compared here is the most common experiment, where the powder was fired at 1000 °C for one hour, the operating temperature was 350 °C and the powders were printed on a multiple electrode device. The response on the small electrode gap is used to compare these devices.

As can be seen from figure 4.21, composition has a small effect on the response of these sensors, and the majority of these devices vary very little as the titanium content is increased throughout the series. You should not expect to see microstructure variation on these sensors for each individual preparation method as all the powders have been fired at the same temperature and for the same length of time. But you should expect to see slight variation in microstructure due to different preparation methods, and this causes slight change in the response of these sensors.

The four sensors that stand out in terms of their response are the two samples that were prepared by method three (Ti/(Ti+Cr)% = 6.34 & 14.464, points E&F respectively) where they exhibit an unusually high response due to their highly porous structure (figure 3.20c&b). The other two devices were prepared by method two (Ti/(Ti+Cr)% = 4.424 & 6.404 point G&H respectively) and show a significantly small response, that is again due to their microstructure, but this time it is because the structure is highly agglomerated and large clusters have formed about five micrometers in size (figure 3.11c&f).
As for the composition effect, only two samples stand out, first is the device prepared by method three (Ti/(Ti+Cr)% = 14.464 point F) and has an unusually high titanium content of 8.54% which also might be attributed to its high response along with its microstructure. The second sample was prepared by method two (Ti/(Ti+Cr)% = 0.331 point K) and has a titanium content of only 0.17% which means it is virtually Cr₂O₃, and this is probably the reason why the response is very low for this device.

There is a general trend for response to increase with titanium content, this effect seems more marked for acetone, ethanol and ammonia then it does for carbon monoxide and water vapour. The “devices” which appear to show responses smaller or larger than expected do not show this effect for all the gases.
Figure 4.21. Response as a function of composition for some of the sensors prepared by methods 1, 2 and 3.
4.7 EFFECT OF ALUMINA ADDITION TO CHROMIUM TITANIUM OXIDE

4.7.1 GENERAL

This set of experiments were performed in order to establish if alumina coming from the substrate and reacting with the chromium oxide layer has any effect on the response of the sensors.

The chromium titanium oxide was prepared using method one described in chapter two, the aluminium oxide (Aldrich) was substituted into chromium oxide \([\text{Cr}_{1.8 \times} \text{Ti}_{0.2} (\text{Al}_2\text{O}_3)_x \text{O}_3],\) where \(x = 0.1\) to 0.3\] and then fired at \(1000^\circ\text{C}\) for one hour.

X-ray powder diffraction was performed on all three fired powders (figure 4.22), as we can see a solid solution has formed between the oxides and we only observe the \(\text{Cr}_2\text{O}_3\) phase.

We know from previous work that aluminium oxide and chromium oxide form a solid solution when sintered at high temperatures, especially as both aluminium and chromium oxide have the same crystal structure.\(^{67}\)
Figure 4.22. X-ray diffraction pattern of \([\text{Cr}_{1.8-x} \text{Ti}_{0.2} (\text{Al}_2\text{O}_3)_x \text{O}_3]\), where \(x = 0.1\) to 0.3] sintered at 1000 °C for one hour and prepared by method one.
4.7.2 GAS RIG RESULTS

As we can see from figure 4.23, the substitution of alumina has significant effect on the response of the sensors. For carbon monoxide and ammonia we see an increase in response as we go from the unsubstituted sample to the substituted one; no significant change in response is observed when further alumina is substituted in. While the response to relative humidity shows a decrease in response as we go to the substituted sample, there is insignificant variation in response as more alumina is substituted in. Ethanol on the other hand shows surprisingly virtually the same response on all three electrodes (no concentration gradient) for the unsubstituted sample, but once alumina is substituted into the oxide material we observe a reverse concentration gradient (figure 4.24).

The concentration gradient (figure 4.24) for carbon monoxide, ammonia and relative humidity show an increase as we go from the unsubstituted sample to the substituted one; no variation in concentration gradient is observed as more aluminium is substituted in the structure.

It is obvious from the above that alumina substitution has a significant effect on both the response and the concentration gradient especially as we go from the unsubstituted sample to the first substituted sample in the series. This leads to say that some of the unusual behaviour that we have observed in the later chapters are probably attributed to both the migration of fluxes from the gold electrodes to the oxide layer that was described earlier and the alumina interaction with the oxide.
Figure 4.23. Response to \([\text{Cr}_{1.8-x}\text{Ti}_{0.2}(\text{Al}_2\text{O}_3)_{x}O_3]\), where \(x = 0.1\) to 0.3\] for four test gases operated at 350 °C.
Figure 4.24. Concentration gradient to $[\text{Cr}_{1.8-x}\text{Ti}_{0.2}(\text{Al}_2\text{O}_3)_x\text{O}_3]$, where $x = 0.1$ to 0.3] for four test gases operated at 350 °C.
CHAPTER FIVE

DISCUSSION OF RESULTS
CHAPTER FIVE

DISCUSSION OF RESULTS

5.1 SUMMARY

The original idea of this piece of work was to investigate the properties of chromium titanium oxide powder. It was thought that by varying the preparation method, the microstructure and possibly the surface composition of the oxide powder would be varied. The effects of changing the titanium concentration and the firing temperature were explored.

Four different preparation methods were used. The first was based on the addition of chromium oxide prepared through the ammonium dichromate route to commercial titanium dioxide. The second method was a colloidal preparation, by adding a colloidal suspension of hydrated chromium oxide to a similar suspension of titanium oxide. In the third method, surfactant was added to the suspension (method two) to help dis-agglomerate the grains. The fourth method was based on the addition of chromium oxide (ammonium dichromate method) to a colloidal suspension of hydrated titanium oxide.

Various physical techniques were used to help understand the properties of the oxide. X-ray powder diffraction (XRD) was used to confirm that the chromium oxide has formed a solid solution with the titanium oxide. It also showed that there was insignificant peak shift for one of the chromium oxides peaks situated at \( \theta \sim 24.5^0 \).
XRD was also used to estimate the crystallite size of the powders. It was found, as expected, that the crystallite size generally increased as the firing time and temperature was increased. There was insignificant variation in size with composition if the sintering conditions were constant.

Scanning electron microscopy images gave not only a visual estimation of the crystallite and grain size, but also more intricate details about the microstructure of the solids. It showed how these structures developed as the firing time and temperature was changed, and how the small nanometer size crystals grew larger, to form larger grain structures, sometimes up to five micrometers in diameter as the firing time and temperature was increased.

There were some exceptions: in particular instances, although the individual grains were very small, large numbers agglomerated together to form very large structures ~ 5μm in size (figure 3.11).

Electron Probe Micro Analysis (EPMA) measurements were able to establish accurate concentrations of the powders. Some of the preparation methods were less predictable in the stoichiometry than others.

Composition maps (EPMA) of sectioned sensor devices showed that certain bonding agents which were used in the printing of the gold electrodes on the substrate had migrated into the oxide layer. The concentration of these bonding agents was dependent on the temperature used to fire the oxide powder onto the substrate, to form the sensor. It appeared that these fluxes affect the response of the sensors, especially near the base of the sensor.
X-ray Photoelectron Spectroscopy (XPS) showed titanium segregation to the surface of the oxide. Generally this effect increased with increasing firing temperature and time. The response of the sensors to certain test gases was generally increased as the titanium content was increased throughout the series, apparently correlating with the increase of titanium concentration at the surface.
5.2 DISCUSSION

In order to separate-out and understand the effects of microstructure and surface composition on response, multiple electrode devices were used in making the sensors (chapter one).

The results showed an unusual gas response law in comparison to the 'commercial' preparation. They also showed no gradient for ammonia, acetone and ethanol, despite the fact that these gases decomposed rapidly on the heated oxide surface, and an inverse concentration gradient for carbon monoxide. So why are we observing these unusual phenomena? Some possibilities are:

1. It might have been due to some aspect of the design of the devices. That is the gas concentration gradient was very large so there was almost no signal on the small gap itself. Instead, this behaved simply as a parallel resistor, with the signal derived from the corner bounded by the connection tab and the common electrode.

2. It could also be due to the microstructure of the oxide layer. Appendices A (method one, Ti/(Ti+Cr) = 5.34%, substrate fired at 700 °C) and B (method one, Ti/(Ti+Cr) = 5.34%, substrate fired at 900 °C) shows highly magnified cross sectional areas of a sensor looking from the base of the electrode (small gap) to the top of the oxide layer. Large pores, which could be a major transport route for the gas, and very fine pores, which lead into agglomerates, which are sealed from the gas are seen. This is despite the lack of agglomeration on the surface of the oxide as observed under the electron microscope. We can also observe that the number and size of these pores increased as the temperature at which the oxide was fired onto the substrate was increased from 700 to 900 °C.
The interpretation then would be that most of the gas gets down a few very large pores, which means that the gas does not completely burn, and only the material around the large pores changes in resistance.

Both the above effects point to a model that looks like this:

\[ R_1 \quad \text{Interior of agglomerates, gas insensitive.} \\
R_2 \quad \text{Exterior of agglomerates and the network surrounding them of a more open structure, gas sensitive.} \]

This model applies equally to all electrode gaps, and if the gas sensitive resistor gets too large then all that is observed is the gas insensitive resistor (figure 5.1). A reasonable interpretation of all the results can be derived from this model.

The expected response law from the literature is:

\[(R/R_0)^2 - 1 = kc\]

Where:

\[ R_0 = \text{base line resistance} \]
\[ k = \text{sensitivity parameter} \]
c = gas concentration

To take account of the effect of agglomerates, one would therefore write, with the notation above:

\[(R_2 / R_{0,2})^2 - 1 = kc\]

And the measured resistance, R is then:

\[1/R = 1/R_1 + 1/R_2\]

The net result is a response law which follows, approximately:

\[R = R_0 (1+kc)^\beta\]

Where the response exponent, \(\beta < 0.5\) and the resistance reaches a limit \(R = R_1\) as the gas concentration increases.

Figure 5.1. Gas response law.
This model explains the basic features of the response and is consistent with the cross-sectioned micrographs. The results showed that the general trend for acetone, ethanol, ammonia and carbon monoxide was a slight increase in response as the titanium concentration was increased across the series. This effect was most marked for acetone and the least marked for carbon monoxide (figure 4.21). These powders had all been fired at the same temperature and for the same length of time. The only difference was the way in which these powders had been formed and mixed initially.

Figure 4.21 also shows that the increase in titanium concentration has virtually no effect on the relative humidity response, apart from points E and F (method three, Ti/(Ti+Cr) = 6.34 & 14.46 % respectively), where there was an unusually high response. The reason for this could be an effect of the diffusion of the gas within the agglomerates and how some gases can penetrate agglomerates better than others depending on the microstructure of the oxide (SEM images of devices E & F are shown in figure 3.20 c & b respectively).

It is notable that water vapour consistently showed response order, $\beta$, significantly larger than the value obtained from other gases. It was as if water vapour could penetrate the very fine pores accessing the interior of the agglomerates whereas the other gases could not. Two effects could be significant: first, water vapour does not burn on the surface of the oxide whereas the other gases all do, to different degrees. The other gases could all be decomposed, to different degrees, near the entrance of the very small pores. Second, diffusion within very narrow pores is determined by the interaction of the gas with the surface of the pores. Water vapour is a much more polar gas than acetone, ethanol or carbon monoxide and is expected to have rather different interaction with the oxide surface.
This work has revealed another important factor, superimposed upon the effects described above. This is the effect of gold electrode interaction with the metal oxide layer. There are low concentrations of certain bonding agents that are added to the gold electrode during manufacturing. This work has shown that these migrate into the metal oxide layer as the oxide is fired onto the substrate and that their concentration and distribution in the oxide layer is dependent on the substrate firing temperature. Cadmium and copper were particularly found in the sensor layer.

The most notable effect that might be attributable to the migration of cadmium and copper from the substrate is the significantly larger response to carbon monoxide found on the small and medium gap electrodes compared to the large, 'inverse gradient' referred to earlier. The narrow gaps sample the response near the electrodes whilst the wider gap averages the behaviour of the whole layer. In the absence of any obvious variation in microstructure, it seems reasonable to attribute the effect to the migration of the bonding agents from the electrodes.

There was a significant increase in response to ethanol as the substrate firing temperature was increased from 750 to 900 °C (figure 3.24). Again this effect was only observed on the small and medium gap electrodes, as for carbon monoxide, and consistent with an effect of bonding agents migrating from the electrodes.
5.3 CONCLUSION

Work from this thesis has revealed that there is a dominant effect of the microstructure on the response of the sensors. It has also shown that it is not sufficient just to prepare fine powders, as agglomerations of these powders must be avoided not only in the powder preparation but also in the preparation of the ink and in the process of printing and firing onto the substrate.

The model proposed in this work shows that a minor part of the structure is gas-sensitive and a major part, the agglomerates, is gas-insensitive and gives a satisfactory rationalisation of results. From the results, it was shown that the water vapour behaves differently to other gases, perhaps because it is able to diffuse into the very fine pores penetrating the agglomerates.

The results also showed that the titanium dissolves in the chromium oxide forming a solid solution phase. The titanium is surface segregated to a significant degree and this segregation increases with increase in firing temperature. Increase of titanium content in the oxide powder does cause a small increase of gas response. Bonding agents especially cadmium and copper, probably as silicates, migrate from the gold electrodes and appear to affect the response.
REFERENCES
REFERENCES

4. N. Taguchi, Japan patent 50-23317 (1969)
5. K. Ihokura, Fachbeichte 93, 32 (1985)
REFERENCES

35. D. E. Williams, UK pat. GB2256055, (1992)
REFERENCES

Appendix A. Highly magnified cross-section area of a sensor looking from the base of the electrodes (small gap) to the top of the oxide layer (sample prepared using method one, Ti/(Ti+Cr) = 5.34%, substrate fired at 700 °C).
Appendix B. Highly magnified cross-section area of a sensor looking from the base of the electrodes (small gap) to the top of the oxide layer (sample prepared using method one, Ti/(Ti+Cr) = 5.34%, substrate fired at 900 °C).