

Electron Spectroscopic Studies of Ti and Co-Ti Alloys.

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Abstract

This thesis is concerned with the room temperature oxidation of Ti metal and three Co-Ti alloy compositions, as studied by high resolution electron energy loss spectroscopy (HREELS) and x-ray photoelectron spectroscopy (XPS) and other electron spectroscopic techniques.

The Ti surface exposed to moderate doses of O_2 is inhomogeneous. XPS indicates the oxide overlayer contains both the monoxide TiO and sesquioxide Ti_2O_3 , but the dioxide TiO_2 becomes dominant at the highest exposures. HREEL spectra of the prepared Ti(0001) surface show loss peaks due to H contamination. The Ti(0001) surface exposed to very small O_2 doses exhibits a sharp loss feature at 65meV. Further exposure results in disappearance of the clean surface 1x1 LEED pattern and growth of a feature at 90-95meV. HREEL spectra of the moderately oxidised Ti(0001) surface and $TiO_2(110)$ show an identical loss feature at 95meV, but in all other respects the spectra are different. The oxidised Ti spectra do not show the distinct phonon loss structure characteristic of $TiO_2(110)$.

A study of the sputtering of single crystal CoTi(110) shows preferential removal of Ti atoms by Ar^+ ion bombardment. Surface segregation of Ti is observed at elevated temperatures. Changes in the surface composition induced by sputtering were followed by Auger electron spectroscopy (AES).

Oxidation of CoTi and polycrystalline Co_3Ti and $CoTi_2$ was examined by XPS and suggests only the Ti component oxidises upon moderate O_2 exposure, and this proceeds in a similar way to Ti metal. Oxygen induced Ti surface segregation is observed. In contrast to O_2 exposed polycrystalline Co, no Co oxides are detected at the alloy surfaces. However, subtle changes occur in the alloy Co core level XPS spectra during oxidation. HREEL spectra of the oxidation of CoTi develop in a similar manner to those of Ti metal.

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List of Contents

Abstract	2
Acknowledgements	3
List of Contents	4
List of Figures	9
List of Tables	14
Notes	15

1. Introduction

1.1	Historical Background	16
1.2	Fusion Research	17
1.3	Storage Devices	19
1.4	Hydrogen Storage Materials	19
1.5	Titanium Intermetallic Alloys	21
1.6	Previous Studies of CoTi	23
1.6.1	Bulk Properties	23
1.6.2	Surface Studies	26
1.7	Previous Studies of FeTi	27
1.8	The Interaction of Hydrogen with Titanium	27
1.8.1	Titanium Oxides	27
1.8.2	Titanium Metal	28
1.9	The Oxidation of Co and Ti	29
1.10	Motivation and Scope of the Present Work	30
1.11	References	32

2. General Principles of Electron Spectroscopy

2.1	Introduction	36
2.2	Surface Sensitivity	37
2.3	X-ray Photoelectron Spectroscopy (XPS)	38
2.3.1	Primary Structure	38
(i)	Multiplet and Exchange Splitting	42
(ii)	Core Level Chemical Shifts	44
2.3.2	Fine Structure	45

(i)	X-ray Satellites	45
(ii)	Shake-up, Shake-down and Shake-off	45
(iii)	Electron-Hole Excitations	47
2.4	The Probability of Interaction: Ionisation Cross-section	47
2.5	Effect of Take-off Angle in XPS	47
2.6	Ultra-violet Photoelectron Spectroscopy (UPS)	48
2.7	Auger Electron Spectroscopy (AES)	49
2.8	Low Energy Electron Diffraction (LEED)	51
2.9	Electron Energy Loss Spectroscopy (EELS and HREELS)	52
2.9.1	An Introduction to Dipole Scattering	53
2.9.2	Dipole Theory of One-phonon Excitation	54
2.10	References	55

3. Experimental Methods: Vacuum System Design and Sample Treatment

3.1	The Importance of Ultra-High Vacuum	59
3.2	General Spectrometer Features and Construction	60
3.3	Excitation	60
3.3.1	X-ray Sources	62
3.3.2	Ultra-violet Photon Sources	62
3.4	Electron Sources	63
3.5	Electron Energy Analysers	63
3.5.1	Hemispherical Designs	63
3.5.2	Resolution	64
3.5.3	Cylindrical Sector Designs	65
3.5.4	Retarding Field Analysers	66
3.6	The Vacuum Generators ESCALAB System	66
3.6.1	Introduction	66
3.6.2	Surface Analysis Facilities	67
3.6.3	Calibration	69
3.6.4	Sensitivity Factors for Quantitative XPS	71
3.7	The Leybold-Heraeus HREELS System	71
3.7.1	Surface Analytical Facilities	75
3.7.2	The ELS-22 Construction	75
3.7.3	Calibration	78
3.8	The Inverse Photoemission (IPES) System	78

3.8.1	Sensitivity Factors for Quantitative AES	79
3.9	Sample Mounting and Pretreatment	80
3.9.1	The Samples	80
3.9.2	Mounting	81
3.10	References	89

4. The Oxidation of Ti Metal

4.1	Surface Preparation	90
4.2	The Oxidation of Ti Followed by XPS	93
4.3	The Surface of Perfect and Defected TiO ₂	93
4.4	Characterisation of Ti Oxides formed on Ti metal	96
4.5	Valence Band Features	98
4.6	A Consideration of Previous Work	100
4.7	Peak Fitting of Ti:2p Structure	106
4.8	Hydrogen Contamination on the Ti(0001) Surface	108
4.8.1	The Hydrogen Binding Site	108
4.9	The Oxidation of Ti(0001) Followed by HREELS	112
4.9.1	Small Oxygen Doses (<1L)	112
4.9.2	Evidence for Subsurface Oxygen	112
4.9.3	Larger Oxygen Exposures	117
4.10	Conclusions	120
4.11	References	124

5. The Sputtering Behaviour of CoTi

5.1	The Polished CoTi Surface	127
5.2	Subsequent Atmospheric Exposure	130
5.3	Sputtering of CoTi Determined by AES	132
5.4	The Effect of Incident Ion Energy	138
5.5	Annealing Behaviour	141
5.5.1	Surface Segregation	144
5.6	Theories of Sputtering	146
5.7	Accounting for the Sputtering Behaviour of CoTi	149
5.7.1	Mass Considerations	149
5.7.2	Bonding Considerations	152
5.8	Comparisons with FeTi	153

5.9	Removal of Contamination from CoTi	154
5.10	Conclusions	154
5.11	References	155

6. The Oxidation of CoTi

6.1	Introduction	158
6.2	The Oxidation of Annealed CoTi Followed by XPS	158
6.2.1	Ti:2p	159
6.2.2	O:1s and C:1s	159
6.2.3	Co:2p	166
6.2.4	Valence Band Spectra	166
6.3	The Oxidation of Sputtered CoTi followed by XPS	170
6.3.1	Ti:2p	170
6.3.2	Co:2p and O:1s	172
6.4	The Oxidation of Co Metal	172
6.5	HREELS of the Interaction of Annealed CoTi with O ₂	175
6.6	Discussion	175
6.6.1	Previous Studies of Co Oxidation	175
6.6.2	The Chemical Shifts of Co Oxides	180
6.6.3	Satellite Structure in Co Oxides	183
6.7	The Oxidation of Annealed CoTi	185
6.7.1	The Co Component	185
6.7.2	Oxygen Induced Ti Segregation in CoTi	185
6.7.3	Spectral Subtraction and Curve Fitting the Ti:2p Spectra	188
6.7.4	Characterisation of Oxides on Annealed CoTi	190
6.7.5	Titanium Sub-oxide Concentration	200
6.8	The Oxidation of Sputtered CoTi	200
6.9	Chemical Shifts in Alloys	203
6.10	HREEL Spectra of CoTi Oxidation	208
6.11	The Oxidation of Related Materials	209
6.12	Conclusions	211
6.13	References	213

7. Further Studies of the Co-Ti Alloy System: Co_3Ti and CoTi_2

7.1	Surface Preparation of Co_3Ti and CoTi_2	216
7.2	The Oxidation of Co_3Ti	219
7.3	The Oxidation of CoTi_2	219
7.4	Valence Band of Co-Ti Alloys	228
7.5	Co Satellite Intensities in Co-Ti Alloys	232
7.6	Studies of Ni Satellites in XPS: Extension to CoTi	236
7.7	Conclusions	239
7.8	References	241
Erratta		242

List of Figures

- 1.1 Diagrammatic representation of hydrogen atoms dissolved in a metallic matrix.
- 1.2 CoTi phase diagram.
- 1.3 Pressure desorption isotherms for the CoTi-H system.

- 2.1 The 'universal curve' of electron escape depth for a particular photoelectron kinetic energy.
- 2.2 Schematic of three types of electron spectroscopy.
- 2.3 Diagram illustrating the decay of a core hole *via* the emission of an electron (Auger process) or a photon (x-ray fluorescence).
- 2.4 A typical XPS spectrum.
- 2.5 Diagram of the Auger emission process.
- 2.6 Illustration of the dipole scattering mechanism, the dipole selection rule and the origin of the scattering lobe in HREELS.

- 3.1 A simple ultra-high vacuum chamber.
- 3.2 Drawing of the Vacuum Generators ESCALAB vacuum system.
- 3.3 XPS spectrum of the Ag:3d region used to calibrate the ESCALAB spectrometer.
- 3.4 Drawing of the Leybold-Heraeus vacuum chamber housing the HREELS spectrometer.
- 3.5 Rear view of the Leybold-Heraeus chamber.
- 3.6 Schematic of the ELS-22 HREELS optics.
- 3.7 X-ray diffraction patterns obtained from the fabricated Co_3Ti and CoTi_2 alloys.
- 3.8 Photographs of the Co_3Ti and CoTi_2 alloy buttons and the Ti(0001) single crystal used in this work.
- 3.9 Drawing of the sample mounting arrangement used in the Leybold-Heraeus chamber.
- 3.10 Photographs of the complete sample mount.

- 4.1 Core level Mg XPS spectra of Ti foil after heating in vacuum to 600°C for 24 hours.
- 4.2 1x1 LEED pattern obtained from the annealed Ti(0001) surface.

- 4.3 Core level XPS spectra of clean and oxidised Ti foil surface.
- 4.4 Detail of the changes in the Ti:2p region of XPS spectra of Ti foil upon O₂ exposure.
- 4.5 Ti:2p and O:1s core level XPS spectra of perfect and defected TiO₂(110).
- 4.6 X-ray excited valence band spectra of the valence regions of clean and oxidised Ti metal foil and TiO₂.
- 4.7 Ti:3p XPS spectra of clean and oxidised Ti foil.
- 4.8 Band picture diagram for Ti metal and slightly defective TiO₂.
- 4.9 Comparison of the synthesised Ti:2p_{3/2} spectra of defected TiO₂ and oxidised Ti.
- 4.10 HREEL spectra of an H-contaminated Ti(0001) surface exposed to D₂.
- 4.11 HREEL spectra of a well annealed Ti(0001) surface exposed to H₂.
- 4.12 HREEL spectra of a Ti(0001) surface exposed to very small doses of O₂.
- 4.13 Disappearance of LEED pattern of clean Ti(0001) with very small oxygen doses.
- 4.14 HREEL spectra of the Ti(0001) surface exposed to O₂ at room temperature.
- 4.15 HREEL spectra of the Ti(0001) surface exposed to moderate and large doses of O₂ at room temperature.
- 4.16 Variation of loss feature intensity and energy observed in HREEL spectra of oxygen exposed Ti(0001).
- 4.17 HREELS of the TiO₂(110) surface.

- 5.1 Core level XPS spectra of polished CoTi, prior to *in vacuo* treatment.
- 5.2 Core level XPS spectra of polished CoTi after sputtering for 30 minutes in the vacuum chamber.
- 5.3 Core level XPS spectra of the air exposed CoTi surface.
- 5.4 Derivative N'(E) AES spectra of the air exposed CoTi surface for different Ar⁺ sputtering durations.
- 5.5 Changes in the peak-to-peak height of features observed in the AES spectra of CoTi during sputtering.
- 5.6 Integral N(E) Auger spectra of the 170 minute Ar⁺ sputtered and air exposed CoTi surface.

- 5.7 Detail of the N(E) and N'(E) Ti LMM region of the 170 minute Ar⁺ sputtered and air exposed CoTi surface.
- 5.8 Auger spectra of Ti, TiO and TiO₂.
- 5.9 Changes in the surface composition of CoTi caused by different Ar⁺ ion sputter energies.
- 5.10 Effect of annealing temperature on Ti surface segregation in CoTi.
- 5.11 Effect of annealing temperature on the O:Ti ratio of CoTi.
- 5.12 Diagram showing recoil sputtering and ion channelling in single crystal materials.

- 6.1 Changes in the Ti:2p normal emission XPS spectra of annealed CoTi with O₂ exposure.
- 6.2 Changes in the Ti:2p grazing emission XPS spectra of annealed CoTi with O₂ exposure.
- 6.3 XPS spectra of the O:1s peak for annealed CoTi with increasing oxygen exposure measured at normal and grazing take-off angle.
- 6.4 Differences in the Co:2p core level XPS spectra of annealed and oxygen exposed CoTi measured at normal emission.
- 6.5 Differences in the Co:2p core level XPS spectra of annealed and oxygen exposed CoTi measured at grazing emission.
- 6.6 Mg K α excited valence band spectra of annealed CoTi and oxidised CoTi.
- 6.7 Changes in the Ti:2p normal emission XPS spectra of sputtered CoTi with O₂ exposure.
- 6.8 Changes in the Co:2p XPS spectra of sputtered CoTi with O₂ exposure.
- 6.9 The Co:2p and O:1s regions of clean polycrystalline Co and Co exposed to 7500L O₂.
- 6.10 Detail of Co:2p XPS spectra of clean and oxidised Co metal.
- 6.11 Valence band region of clean and oxidised Co metal.
- 6.12 HREEL spectra of annealed CoTi exposed to O₂.
- 6.13 Relative intensity of HREELS loss features observed on Ti(0001) and annealed CoTi with oxygen exposure.
- 6.14 Diagram illustrating the origin of satellite structure observed in the photoelectron spectra of Co oxides.

- 6.15 Intensity of inelastic background versus $\text{Co:2p}_{3/2}$ height for annealed CoTi with oxygen exposure.
- 6.16 Variation of the Co:2p , O:1s and C:1s XPS intensity ratios relative to Ti:2p for O_2 exposed CoTi.
- 6.17 Contrasting Ti:2p peak shape and XPS binding energy for CoTi and polycrystalline Ti.
- 6.18 $\text{Mg K}\alpha$ Ti:2p XPS spectra measured at 15° take-off angle for annealed CoTi showing difference data for annealed and oxygen exposed CoTi surfaces.
- 6.19 $\text{Mg K}\alpha$ Ti:2p XPS spectra measured at 90° take-off angle for annealed CoTi showing difference data for annealed and oxygen exposed CoTi surfaces and that of clean and oxidised Ti metal.
- 6.20 Examples of curve-fitting of Ti:2p region of XPS spectra.
- 6.21 Concentration of Ti suboxides at the oxidised CoTi surface.
- 6.22 Variation in the Co:2p , O:1s and Ti:2p XPS peak intensities for sputtered CoTi with oxygen exposure.
- 6.23 Ti:2p region of the sputtered CoTi surface measured at three different emission angles.
- 6.24 $\text{Mg K}\alpha$ Ti:2p XPS spectra measured at 90° take-off angle for sputtered CoTi showing difference data for sputtered and oxygen exposed CoTi surfaces.

- 7.1 The Ti:2p XPS spectra of air exposed CoTi, Co_3Ti and CoTi_2 .
- 7.2 Co:2p XPS spectra of air exposed CoTi, Co_3Ti and CoTi_2 .
- 7.3 Changes in the Ti:2p region of annealed Co_3Ti upon exposure to O_2 .
- 7.4 $\text{Mg K}\alpha$ Ti:2p XPS spectra measured at 90° take-off angle for annealed Co_3Ti showing difference data for annealed and oxygen exposed surfaces.
- 7.5 Changes in the Ti:2p region of annealed CoTi_2 upon exposure to O_2 .
- 7.6 $\text{Mg K}\alpha$ Ti:2p XPS spectra measured at 90° take-off angle for annealed CoTi_2 showing difference data for annealed and oxygen exposed surfaces.
- 7.7 Variation of the Co:2p , O:1s and Ti:2p XPS peak intensity for Co_3Ti and CoTi_2 with oxygen exposure.
- 7.8 $\text{Mg K}\alpha$ excited valence band spectra of Co, Co_3Ti , CoTi, CoTi_2 and Ti.

- 7.9 Detail of the metal:3d structure around the Fermi level of Co, Co₃Ti, CoTi, CoTi₂ and Ti.
- 7.10 Binding energy of d band maximum and intensity at E_F for Co, Co₃Ti, CoTi, CoTi₂ and Ti.
- 7.11 Calculated DOS for CoTi.
- 7.12 XPS spectra of the Co:2p_{3/2} peak for Co-Ti alloys, showing changes in satellites feature intensity.
- 7.13 Band picture diagram for Ni and Ni alloys.

List of Tables

- 2.1 X-ray satellites of anode materials.
- 3.1 Sensitivity factors for Mg K α XPS.
- 3.2 X-ray diffraction patterns from annealed CoTi₂ and Co₃Ti alloys.
- 3.3 Characteristic d spacings of Co-Ti-O materials.
- 4.1 Ti:2p_{3/2} and Ti:3p XPS binding energies.
- 4.2 Vibrational frequencies for O and H at three-fold hollow sites of various substrates.
- 5.1 Auger electron energies compiled from literature.
- 6.1 Some XPS data for Co and Co oxides.
- 7.1 XPS binding energies of the Ti (0):2p_{3/2} peak in Ti and Co-Ti alloys.

Notes

- (i) The Y axis on all spectra indicates 'Intensity' in arbitrary units (a.u.) unless stated otherwise.
- (ii) All quoted XPS energies are in electronvolts (eV) and refer to binding energy relative to the Fermi energy E_F . The binding energies of core level photoelectron peaks relate to the position of the peak maximum and not to the position of the peak centre at half-height unless otherwise stated.
- (iii) All quoted HREELS loss energies are in millielectronvolts (meV) and are referenced to the elastic peak energy. Where appropriate, wavenumber (cm^{-1}) conversions are included. All HREEL spectra shown here were measured in the 'specular direction', that is, with incident angle θ_i approximately equal to the scattered angle $\theta_s \approx 60^\circ$ from the surface normal.
- (iv) $K\alpha_{3,4}$ x-ray satellite contributions have been removed from all XPS spectra unless stated otherwise.

1 Introduction

1.1 Historical Background

Ever since the discovery over a hundred years ago that Pd can accommodate large quantities of hydrogen as interstitial atoms, there has been considerable interest in the behaviour of hydrogen in metals and at metal surfaces. Hydrogen is the smallest atom that can be dissolved in a metallic host and its small mass and large interaction with the host electrons and nuclei are responsible for many unusual solid state effects^{1,1}. A number of areas of technological importance have prompted fundamental investigation: catalysis, fission and fusion nuclear energy, corrosion science, brittle fracture in metallurgy, magnetism, superconductivity, and energy storage systems. More specifically, the surfaces of metal-hydrogen systems have been investigated with respect to surface phase stabilities, segregation, surface reconstructions and the absorption/adsorption mechanism. Obviously, the surface is the point of first contact between the hydrogen molecule and the bulk and so is crucially important in determining hydrogen absorption by a metal.

The rate of hydrogen uptake must depend both on the kinetics of dissociation at the surface and on the rate of subsequent diffusion into the bulk. The surface condition of the metal will determine hydrogen dissociation and adsorption at the surface. The metal surface may be clean, crystalline, amorphous, oxidised or contaminated in some other way whilst the hydrogen may be present as molecular H₂ or atomic H (as in a plasma).

The dynamics of hydrogen diffusion between bulk lattice sites involves both classically activated processes and quantum tunnelling at low temperatures. As an additional electron and proton are accommodated in the metal lattice, the host electronic structure is changed. Changes may manifest themselves as metal-semiconductor transitions or unusual magnetic effects. On a macroscopic scale, changes in the electronic properties of the host may also lead to mechanical changes, most often embrittlement and structural disintegration.

As hydrogen is absorbed by a metal crystal, the lattice usually expands and H atoms begin to occupy well-defined lattice sites in a random manner. As the hydrogen concentration increases, the lattice becomes strained, disorder-order transitions may occur and hydride phases are formed as shown diagrammatically in figure 1.1. The stability of each phase will have important bearing on the thermodynamics of hydrogen uptake and the ultimate hydrogen concentration in the material.

The hydrogenation of some metals and alloys has been found to cause an increase in the superconducting transition temperature T_c ^{1,2} and, before the emergence of high T_c oxide superconductors, extensive research was conducted on hydrogenated metal systems. For example, Ti metal has a T_c of 0.4K, but by implanting H atoms to a concentration corresponding to $TiH_{0.14}$, T_c can be raised to 4.95K. Elevated transition temperatures of 17K have been recorded for hydrogenated CuPd alloys.

1.2 Fusion Research

Interest in materials which absorb large quantities of hydrogen reversibly has recently been concerned with aspects of fusion research where there is a need for efficient recycling of hydrogen (tritium) at the plasma-containing chamber walls^{1,3, 1.4}. Hydrogen isotopes form the major component of the residual vacuum at the edges of plasmas in traditional experimental fusion devices. Therefore, the interaction of the wall material with these isotopes will have important consequences for the stability of the plasma. Hydrogen recycling is the process whereby hydrogen isotopes leave the main plasma flux, interact with the chamber wall and finally return to the plasma. A number of effects are involved in recycling at the wall including the back-scattering of hydrogen, the adsorption and absorption of hydrogen by the wall and the re-emission of hydrogen into the chamber by thermal or stimulated desorption (sputtering). Hydrogen can remain trapped in the wall material bulk. Hence, the choice of wall material will be critical for controlled hydrogen management in the fusion chamber.

Recent reports of fusion at room temperatures ('cold fusion') in electrochemically deuterated Pd^{1.5} and in gas phase deuterium absorbed by

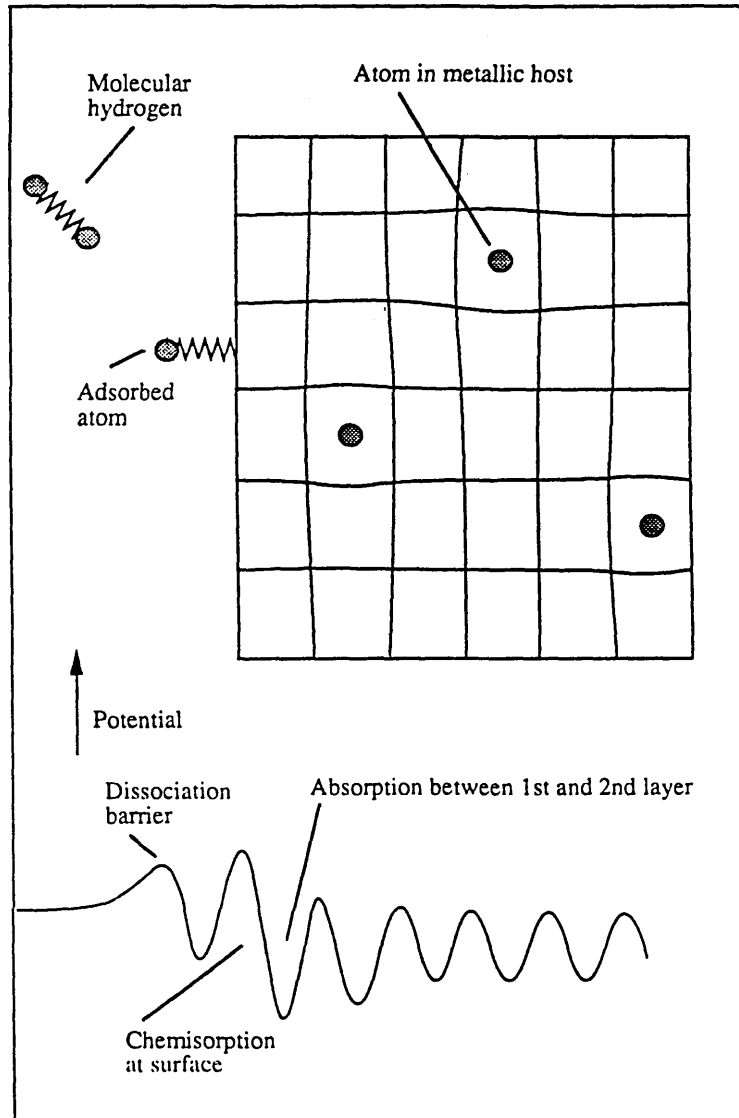


Figure 1.1: Diagrammatic representation of hydrogen atoms dissolved in a metallic matrix. Upon formation of such a solid solution (α phase) the host lattice becomes strained. The variation in potential (hypothetical) on passing through the metal lattice is shown below^{1.15}.

metallic Ti^{1.6} have rekindled awareness of the remarkable behaviour of hydrogen and its isotopes in metals although this effect is now believed to be unrelated to the conventional fusion process^{1.7}. Obviously, an understanding of the gas/metal interface is vitally important in these applications.

1.3 Storage Devices

The development of hydrogen storage vessels, the use of hydrogen absorbing materials for use in fuel cells and the use of such materials for H₂ purification^{1.8} has also attracted some interest. Indeed, one of the most convenient methods of supplying ultra-pure hydrogen is by decomposition of a metal hydride. Several such systems are available commercially. The absorption of a few percent H₂ by weight by a material allows relatively large volumes of gaseous hydrogen to be confined safely in a smaller volume. The release of the hydrogen from the storage material is achieved simply by heating. A commercially viable storage system must allow charge-discharge-recharge to be carried out many hundred times. The evolved hydrogen often has an improved purity compared to that of the initially absorbed gas although initial gas purity is important. Common gas contaminants, in particular O₂, are retained irreversibly in the storage material. Of course, the efficiency of the alloy and its ultimate useful lifetime are then gradually diminished. An overview of the industrial applications of hydrogen storage alloys is given in Bernauer and Halene^{1.8} and references therein.

1.4 Hydrogen Storage Materials

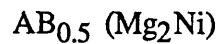
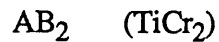
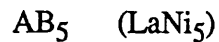
Many clean metal surfaces, including W, Ta, Mo, Ti, Zr, Pd, Rh, Pt, Ba, Nb and Cr, react at room temperature directly with molecular hydrogen^{1.9}. Many transition metals form stable hydrides of well defined phase. The hydride phases are often high temperature variants of the pure metal crystal structure. However, in general the affinity for hydrogen is so great (the enthalpy of hydrogenation is large and negative) that high temperatures are necessary to desorb the hydrogen again. The approximate relationship between hydrogen partial pressure p_{H_2} and the enthalpy of formation of the hydride ΔH_f is given by the van't Hoff relation^{1.4},

$$\frac{1}{2} \ln p_{H_2} = \Delta H/RT - \Delta S/R \quad (1.1)$$

and since ΔS approximately corresponds to the translational entropy loss of gaseous hydrogen ($T\Delta S \approx -65 \text{ kJmol}^{-1}\text{H}$ at 300K) it is practical to simply consider the enthalpy of formation of the hydride. For example, the heat of formation of TiH_2 is approximately $-42 \text{ kJmol}^{-1}\text{H}^{1.10}$, so the temperature necessary to produce a dissociation pressure of 1 bar above the hydride is of the order of 650K. Therefore, any material which is to be considered for potential *reversible* storage purposes must satisfy the two basic constraints of maximum hydrogen absorption together with release of the absorbed hydrogen at sensible temperatures. In practice, a hydrogen dissociation pressure of the order of 1 bar at 300 K corresponds to a heat of hydride formation of about $-19 \text{ kJmol}^{-1}\text{H}^{1.4}$ and thus only those materials with a heat of hydride formation in the region -12 to $-25 \text{ kJmol}^{-1}\text{H}$ are of sufficient *instability* to be potentially useful for hydrogen storage purposes. Such specifications can be met by alloying a metal with a large ΔH_f of the hydride, such as La, Ti, Zr, Ce or Mg with a less reactive metal, for example, Ni, Co, Fe, Mn or Cr.

The discovery of high hydrogen solubility in materials such as $\text{Mg}_2\text{Ni}^{1.11}$, $\text{FeTi}^{1.12}$ and $\text{LaNi}_5^{1.13}$ prompted intense research into absorption by intermetallic compounds and oxygen stabilised compounds such as $\text{Ti}_4\text{Fe}_2\text{O}_x^{1.14}$. Many materials have since been proposed as suitable storage media, but those based upon lanthanum and titanium have proved to be the most popular. More recently, rare-earth based alloys have begun to be studied.

The main differences between intermetallic hydrides and elemental hydrides are a larger range of interstitial sites; a wider stoichiometry range and a thermodynamic stability which can be tailored by substitution; and the formation of alloy hydrides whose elemental metals do not readily react with H_2 . Four major classes of hydrogen storage alloys (representative compound) have been extensively investigated to date.



where B is a generally a group VIII B transition metal (Fe, Ni, Co) and A can be a alkaline earth, an early transition metal, an actinide or rare earth.

Most potential storage alloys are unreactive to hydrogen upon first exposure after fabrication. They need to be 'activated' by exposure to hydrogen at high temperatures and/or pressures. The activation process involves the chemical reduction/solution of oxide overlayers which readily form at the surface under ambient atmosphere. Whilst these oxide layers do not greatly reduce diffusion of H atoms through into the bulk, H_2 dissociation at the surface is inhibited and therefore the ability to take up hydrogen is substantially reduced. Subsequent re-exposure of the activated surface to O_2 (air) passivates ('poisons') the surface again.

As a general observation^{1.15}, those intermetallic alloys based on the rare earth elements are easy to activate and hydrogenate/dehydrogenate but are easily poisoned and physically disintegrate after a few cycles ('decrepitate'). Those alloys based upon an alkaline earth component have a high H capacity per unit mass, but are difficult to activate, absorb hydrogen slowly and must be dehydrogenated at relatively high temperatures. The actinide binary and ternary alloys offer ideal hydrogenation/dehydrogenation behaviour coupled with high H capacity but are expensive.

The Ti intermetallics arguably offer the best compromise hydrogenation characteristics. They are poisoned relatively easily but can be simply reactivated. For example, the binary intermetallic CoTi can be activated by heating to 600K for 20 minutes in 2MPa H_2 allowing the sample to cool in hydrogen. Maximum activity is reached after a few such cycles^{1.16}.

1.5 Titanium Intermetallic Alloys

Titanium hydride is a black brittle solid which has a maximum ideal

stoichiometry of $\text{TiH}_{\approx 2}$ (lattice defects inhibit total hydrogen uptake). At 78K, TiH_2 is tetragonal with a unit cell c/a ratio of 0.945^{1.17}. As the temperature increase, c/a increases smoothly, until at 310K $c=a$ and the structure is cubic. Above this temperature, the length of the cubic cell increases with no apparent discontinuity. Hydrogen occupies mostly tetrahedral sites in Ti at room temperature and the expanded unit cell volume of the hydride increases the Ti-Ti bond length from 2.952Å in Ti to 3.140Å in TiH_2 .

Many binary alloys involving Ti are known to form hydride phases. Titanium metal crystallises in an h.c.p. structure and only absorbs hydrogen slowly at room temperature. A phase transition to a b.c.c. structure with an associated larger free cell volume occurs at 882.5°C^{1.18} and H_2 is absorbed much more rapidly above this temperature. Alloying Ti with various metals can stabilise the b.c.c. arrangement of metal atoms so that hydrogen uptake is rapid at room temperature^{1.19}. Binary titanium alloys proposed^{1.20, 1.21} on the basis of thermodynamic considerations include TiFe, TiNi, TiMn, TiMn_2 , TiCr_2 , TiRe, Ti_3Al , Ti_3Sn and the alloy studied here, CoTi. With a heat of solution of hydrogen of -20 to -27kJmol⁻¹H^{1.16}, CoTi is a simple binary intermetallic which crystallises in the (cubic) CsCl structure. It has potential as a relatively cheap hydrogen storage alloy, forming a solid solution hydride phase with a maximum composition of $\text{CoTiH}_{\approx 1.5}$. CoTi is electronically and structurally similar to FeTi and NiTi, but has received relatively little attention.

Subtle changes in the thermodynamic properties of binary intermetallics may be effected by partial atomic substitution. For example, investigations have been carried out^{1.20, 1.22} on Mn substituted $\text{Co}_{1-x}\text{TiMn}_x$ which has a dissociation pressure of 1 bar at 90°C with $x=0.5$ versus 130°C for CoTi at maximum hydrogen capacity.

However, oxide overlayers on the alloy surface have been shown to reduce substantially the diffusion of hydrogen into the alloy bulk^{1.23, 1.24}. This passivation process can occur as the result of inhibited dissociation of H_2 molecules at the surface or by low permeation rates through the overlayer. There is evidence that the former process is rate limiting in Ti

containing materials (see below). The rate of diffusion of protons in potential storage materials at room temperature is expected to be very high^{1.25}.

1.6 Previous Studies of CoTi

1.6.1 Bulk Properties

There has been relatively little research concentrating on CoTi and much of the literature that has been published has been concerned with bulk properties. The CoTi phase diagram has been compiled by Murray^{1.26} and is shown in figure 1.2. Not surprisingly, it is very similar in general outline to the FeTi phase diagram^{1.27} containing two deep eutectic points. It shows that two other structurally ordered compounds occur in the Co-Ti solid solution system, Ti_2Co and TiCo_3 , both of which are potential storage materials.

Thermodynamic relationships and structural transformations in CoTi and NiTi were investigated by Burch and Mason^{1.16, 1.28, 1.29}. Desorption isotherms show a series of plateaux corresponding to the formation of four separate hydride phases as shown in figure 1.3. For CoTiH_x , the α phase exists up to $x \approx 0.1$, the β phase with $x \approx 0.84$, the γ phase with $x \approx 1.2$ and the δ phase with $x \geq 1.45$. It was suggested that in the β phase, the H atoms sit in the tetrahedral sites of the b.c.c. lattice. At higher H concentrations, H begins to occupy the octahedral sites.

The formation of three b.c.c. binary alloys FeTi, CoTi and NiTi of similar lattice parameter ($a_0 = 5.6239, 5.6446, 5.6654 \text{ \AA}$ respectively^{1.30}) has presented the opportunity for studying the importance of electronic factors in determining the stability and behaviour of intermetallic hydrides. A number of theoretical papers have concentrated on this area^{1.30, 1.31, 1.32}.

Investigation has been further motivated by the observation that both FeTi and CoTi are non-magnetic but the substituted pseudo-binary, $\text{Fe}_{1-x}\text{Co}_x\text{Ti}$ (with $0.25 \leq x \leq 0.65$), is ferromagnetic. The reasons for this unusual magnetic behaviour have not been resolved to date but it is thought likely that anti-site atoms (that is, Co and Fe on Ti lattice sites) are at least partly responsible^{1.33, 1.34}. NiTi alloy has attracted particular attention as a

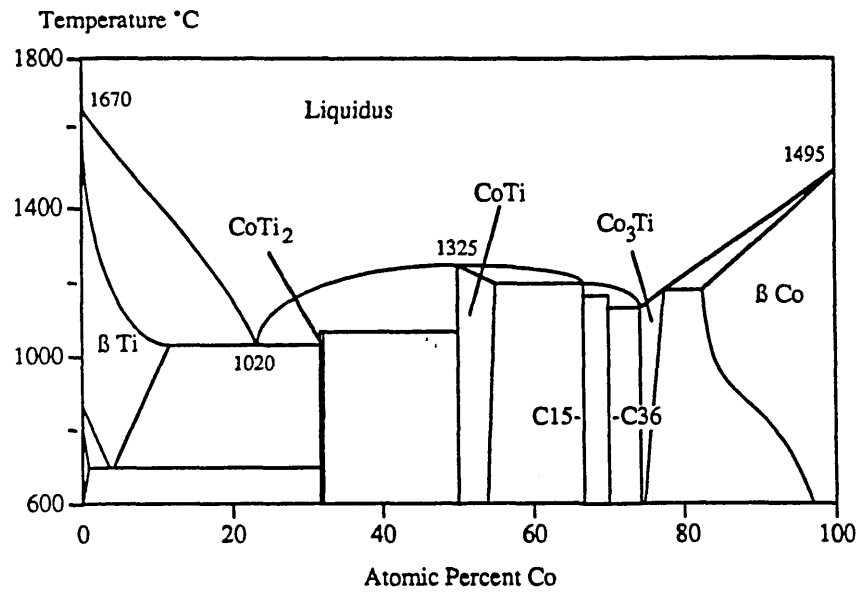


Figure 1.2: CoTi phase diagram^{1,26}. Between pure Co and pure Ti, three ordered compounds exist - CoTi₂, CoTi and Co₃Ti. Two other distinct phases, the C15 and C36 Laves phases, are also indicated.

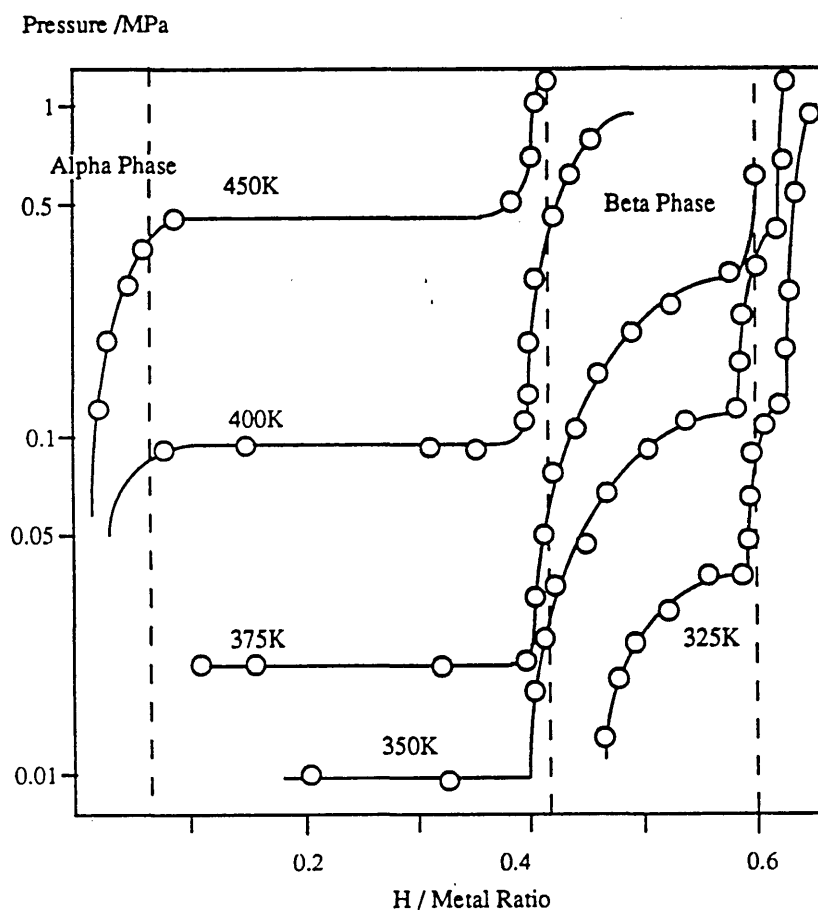


Figure 1.3: Pressure desorption isotherms for the CoTi-H system for a variety of temperatures^{1.28, 1.29}. The α phase exists up to $H/M \approx 0.05$. Further H is accommodated by the formation of a hydride phase (β phase) with $H/M = 0.42$. The two co-exist at intermediate compositions.

result of so called 'shape memory' effects^{1.35}. The alloy exhibits an order-disorder transition at $\approx 40^\circ\text{C}$. If the material is physically deformed below this transition temperature, it regains its original shape if heated to above the transition temperature. The FeTi and CoTi alloys do not show this effect.

X-ray emission spectroscopy (XES) has been used to study the band spectra of FeTi, CoTi and NiTi^{1.36}. Shifts in both the $K\alpha_1$ and $K\alpha_2$ emission lines ($2p_{3/2}$ and $2p_{1/2} \rightarrow 1s$) for Ni and Ti with respect to the elements were recorded for NiTi. Shifts of the Ti $K\alpha$ lines only were observed in CoTi and FeTi. The significance of these measurements will be discussed later.

1.6.2 Surface Studies

To date, there has been relatively little work on CoTi using contemporary surface science techniques. Rivière^{1.37} has obtained a low energy electron diffraction (LEED) pattern from the (110) surface whilst preparing the surface for hydrogenation studies, although the authors note that it was impossible to completely remove O from the surface as revealed by Auger electron spectroscopy (AES) measurements. The Auger spectrum of the CoTi(110) surface showed a weak peak at 70eV not attributable to Auger transitions. Such a peak was assigned to diffraction of the outgoing secondary electrons by comparison with other systems since peak intensity found to be extremely sensitive to surface order, temperature and angular orientation.

Netzer *et al*^{1.38} used AES, LEED and ultraviolet photoelectron spectroscopy (UPS) to study the surface electronic structure of CoTi in relation to band structure calculations. The effects of H_2 and D_2 chemisorption were investigated at 300 and 150K. After ion bombardment, the surface was found to be somewhat Ti-rich, although no adsorbate induced segregation was noted. Hydrogen reacted readily with unannealed and annealed surfaces at both temperatures as indicated by changes in the He I ($h\nu=21.2\text{eV}$) UPS spectra. Intensity growth at 4-9eV in UPS and was assigned to mixed H:1s and Ti:3d states by analogy with data on FeTi and calculated density of states (DOS)^{1.30, 1.31, 1.32, 1.39} for CoTi. In addition,

the calculations on FeTi indicate that metal 4p states lying 1.5eV above the Fermi level E_F are lowered by 3eV upon hydrogenation, resulting in structure at 1.5-2eV below E_F (see below). Similar conclusions were inferred by Netzer *et al* for CoTi.

1.7 Previous Studies of FeTi

FeTi and FeTiH_x has been studied quite extensively by both theoretical and experimental means since this was often considered to be the most promising potential storage material^{1.40}. FeTi also forms a CsCl-type crystal structure that has very similar electronic properties to CoTi, but CoTi accommodates one extra electron and so has a higher density of states at E_F . FeTi dissolves some hydrogen to form the α phase ($\text{FeTiH}_{x \leq 0.1}$) with an expanded CsCl structure^{1.41}. The β_1 phase (FeTiH), β_2 phase ($\text{FeTiH}_{1.4}$) and γ phase ($\text{FeTiH}_{1.9}$) also exist as distorted cubic structures.

Band structure calculations^{1.39, 1.42, 1.43, 1.44} have shown that the Fermi energy lies in the valley between the occupied M-M^s bonding bands (mostly Fe:3d) and the empty antibonding bands (mostly Ti:3d states) in FeTi. Hydrogenation results in the pulling down of both empty states from above E_F and some of the occupied states. Some charge transfer, Ti $\rightarrow$ Fe, has been suggested^{1.45, 1.46} which is manifest as shifts in the core level photoelectron peaks. Studies of FeTi and FeTiH_x will be discussed in greater detail in subsequent chapters.

1.8 The Interaction of Hydrogen with Titanium

1.8.1 Titanium Oxides.

On a perfect TiO_2 surface (rutile or anatase), the adsorption of molecular or atomic H is negligible^{1.47}. A similar pattern emerges for many perfect single crystal oxide surfaces (SrTiO_3 , NiO, WO_3 , ZnO)^{1.48}. However, in the presence of defects at the surface of TiO_2 single crystal, H_2 dissociation is observed below 370K^{1.49}. Evidence for H species bound to Ti to form a Ti-H like bond or to O to form an -OH group has been observed

^s M-M = Metal-Metal, M-H = Metal-Hydrogen

in UPS spectra^{1.50}. Studies have shown that it is inhibited dissociation of molecular hydrogen at the perfect TiO₂ surface that results in its inert behaviour. The diffusion of atomic H through large c-axis oriented channels in the rutile structure is fast^{1.51} but lattice defects were shown to trap H atoms and thus reduce diffusion.

Although the precoverage of transition metal surfaces with electronegative adatoms (O, C, S or Cl) greatly reduces H₂ dissociation at the surface^{1.52}, the effect is less severe on polycrystalline substrates. Drastic reduction of hydrogen uptake has been observed in the case of oxygen exposed polycrystalline Ti surfaces^{1.53} where the oxide film is >20Å thick. Furthermore, hydrogen permeation is completely restored by depositing a thin Ti or Fe overlayer on the oxide surface. Diffusion through the film is unaffected by the presence of a *buried* oxide layer. It was commented that hydrogen reaction is completely terminated by the formation of TiO₂^{1.54}, although work by Fromm *et al* on lightly oxidised Ti^{1.23, 1.55, 1.56} has suggested that reaction probability falls to $\approx 10^{-2}$ of its original value 'upon completion of an oxygen monolayer'. At high temperatures, oxygen dissolves into the Ti bulk, leaving a negligible surface concentration and restoring the surface activity toward hydrogen^{1.57}.

1.8.2 Titanium Metal

Ti metal reacts with hydrogen to form TiH₂ with a CaF₂-type structure. The interaction of H with clean Ti surfaces, both single crystal and polycrystalline, is well documented. In addition to the work cited above, it has been studied with a variety of surface sensitive techniques. AES and quartz crystal microbalance (QCM) measurements on D₂ uptake in thin Ti films^{1.53} were consistent with the formation of saturated TiD₂ films (>1000Å) within 30 minutes at a deuterium pressure of 10⁻⁵torr. Changes were noted in the Ti LMV and LMM peak shapes, especially after spectral deconvolution. The 26eV MVV Auger peak becomes split into a doublet upon exposure to 60L[¶] H₂^{1.58}. Electron energy loss spectroscopy (EELS)^{1.59} indicates a quenching of the Ti surface plasmon at $\approx 8\text{eV}$ loss energy upon exposure to 60L H₂ and the growth of a surface feature at

[¶]1L (Langmuir) = 10⁻⁶torr s

5eV^{1.58}. Similar spectra are presented in work by Burrell and Armstrong^{1.53}.

Photoemission (UPS) spectra of MH_x ($M=Ti, Zr, Hf$)^{1.60} show that the d-band extends to $\approx 3\text{eV}$ below E_F and found that hydrogen induced bands at 5.5eV and 7eV binding energy. Similar results have been obtained by other authors^{1.59, 1.61, 1.62} which note the growth of structure at 5-5.5eV binding energy concluded to be the result of bonding between Ti:3d and H:1s bands. The growth of a feature at -1.4eV was attributed to a localised surface phase on the Ti(0001) surface^{1.62}.

Detailed angle resolved UPS (ARUPS) measurements^{1.63, 1.64} identified H-induced surface states. Comparison was made with the DOS calculated by combining the bonding and antibonding H:1s and Ti:3d and 4s orbitals for particular Ti-H geometries. Results were consistent with other work^{1.65} in giving a minimum total energy for an H atom 0.42Å above the Ti surface plane at the three-fold hollow site.

All Ti core levels of TiH_2 measured by x-ray photoelectron spectroscopy (XPS) were found to shift by 0.5-1eV to higher binding energy with respect to Ti metal. This is consistent with some charge transfer to the H atoms^{1.66}. For example, Riesterer^{1.67} measured a shift of +0.5eV binding energy between Ti and $TiH_{1.9}$, together with changes in the core level lineshapes.

1.9 The Oxidation of Co and Ti

The oxidation of both Co and Ti metal has been studied by a variety of surface techniques but in much of the earlier work, confusing and contradictory reports were made as to the oxidation products.

It has been claimed that TiO ^{1.68, 1.69, 1.70}, Ti_2O_3 ^{1.71} and TiO_2 ^{1.72, 1.73, 1.74} are the oxide products on Ti. Much of the disagreement seems to be related to Auger measurements. Very subtle changes occur in the Auger spectra of Ti with oxidation and the spectra of TiO , Ti_2O_3 and TiO_2 are all very similar. In many cases, the surface O:Ti ratio saturated at 1.0-1.5 naïvely implying TiO or Ti_2O_3 was formed.

Other authors commented that spectral features can be explained by the presence of at least two oxidation products^{1.59, 1.75, 1.76}. Largely as a result of the relatively major changes that occur in XPS core level spectra, and the chemical information obtained from such experiments, it is now generally agreed that the oxidised Ti surface is inhomogeneous. Several sub-oxides are formed on the Ti surface upon exposure to O₂ including TiO, Ti₂O₃ and TiO₂ species with TiO₂ (oxygen deficient at moderate exposures) being the ultimate product.

Similarly, the oxidation of Co metal has been investigated by XPS and AES studies and the oxide surface characterised as CoO^{1.77, 1.78, 1.79}, Co₂O₃^{1.80} and Co₃O₄^{1.81, 1.82, 1.83}.

Detailed XPS studies^{1.84, 1.85} established that CoO is the primary oxidation product when Co is exposed to large doses of O₂, but Co(OH)₂ forms if Co is exposed to air and probably this accounts for the variety of compounds proposed as oxidation products. Detailed comparison of XPS core level lineshapes from oxygen exposed Co metal with standard Co compounds^{1.86, 1.87} including CoO, Co₃O₄, Co(OH)₂ and CoO(OH), concluded that the surface oxide formed after *circa* 10,000L O₂ exposure is predominantly CoO.

The literature relating to Ti and Co oxidation will be discussed in later sections in more detail in the context of the work presented here.

1.10 Motivation and Scope of the Present Work

It has been demonstrated that the oxygen concentration at a metal or alloy surface greatly influences the adsorption/absorption of molecular hydrogen. In some cases, the oxide overlayers occurring on a particular metal surface are reasonably well documented. This is the case for Co and Ti. However, turning to Ti containing potential hydrogen storage alloys, a characterisation of the surface passivation process has not been attempted in a systematic way although many workers make some comment about oxygen at the surface. Hence, this thesis will be largely concerned with a

comparative XPS study of oxidation of the metals Ti and Co in relation to Co-Ti alloys. Three alloy compositions have been studied, namely Co_3Ti , CoTi and CoTi_2 . Comparison will also be made between the behaviour of these materials and closely related alloys using the available literature.

The results show that exposure of CoTi to oxygen results in oxidation of the Ti component alone. Pronounced oxygen induced Ti segregation was found. Oxidation proceeds in a similar manner to that found on elemental Ti, with the formation of an inhomogeneous oxide layer. No oxidation of the Co component could be detected. This can be explained by thermodynamic arguments.

Compositional changes are observed in the course of surface preparation of many alloys. These compositional changes also occur in the CoTi system, where preferential removal of Ti atoms from the surface was found after Ar ion bombardment. Diffusion of Ti to the surface occurred during sample heating. A study of this phenomenon was performed and is in agreement with mass and surface tension models.

Most of the experimental surface specific techniques used to study metal-hydrogen systems cannot detect H directly and results are often inferred. However, high resolution electron energy loss spectroscopy (HREELS) is particularly sensitive to the vibration of H atoms at a surface. HREELS has been used previously to examine the interaction of H with a variety of transition metals^{1.88, 1.89} but there has not been a study of hydrogen on Ti despite the technological importance of this metal. In this work, HREELS was able to directly probe H on the $\text{Ti}(0001)$ surface. From the frequency of this vibration it is possible to comment on the likely binding site. This work was extended to systematically examine the adsorption of oxygen on this surface by HREELS. A search of the literature has revealed only one other report of HREELS applied to O_2 on $\text{Ti}(0001)$ which is limited to the initial stages of oxidation^{1.90}. HREELS work was extended to include a study of the oxidation of $\text{CoTi}(110)$.

Comparison with published relevant data on the oxidation of Co and Ti together with data relating to FeTi will be made throughout.

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2. General Principles of Electron Spectroscopy

2.1 Introduction

In an isolated atom, the relation between the irradiating photon energy $h\nu$ and the kinetic energy of the ejected electron E_k is given by the Einstein equation^{2.1},

$$E_k = h\nu - E_i \quad (2.1)$$

where E_i is the ionisation potential of that electron. Since electrons occupy well defined states of particular energy, by irradiating an atom with photons of sufficient energy and measuring the kinetic energy of the ejected electrons, we immediately have a measure of the energies of these states.

The highest filled level of a band in a solid is called the Fermi energy E_F . The removal of an electron from here to just outside the solid (to the vacuum level E_V) must overcome the solid work function ϕ . The work function is unique to the material, and indeed the crystal face, and can be envisaged as the attractive force felt by the ejected electron as a result of the image force of the 'hole' left behind in the band^{2.2}. Therefore, the minimum energy required by an electron to leave a solid is ϕ , and so the Einstein equation governing photoemission for solids becomes,

$$E_k = h\nu - E_B - \phi \quad (2.2)$$

where E_B is the binding energy relative to E_F . In x-ray photoelectron spectroscopy (XPS), soft x-rays are used to irradiate a solid sample. Commonly used x-rays allow photoelectrons to be ejected from some core and all valence levels. If lower energy ultra-violet radiation is used, the photoelectrons only have sufficient energy to eject valence electrons and the technique is called ultra-violet photoelectron spectroscopy (UPS). Decay of the excited core hole state produced by ionisation can result in the ejection of an x-ray photon (x-ray fluorescence) or a further electron (Auger electron) to produce a doubly ionised atom^{2.3}.

Correlating the ejected electron binding energy with the orbital energy is only an approximation which assumes that the initial electron state energy remain unchanged during the photoelectron emission process. In this 'sudden approximation', first postulated by Koopmans^{2,4}, the final state wavefunction is simply the initial state wavefunction minus one electron. In reality, this Koopmans state is never observed since electrons in other orbitals rearrange as the result of changed Coulomb interactions. The effect is to screen out the positive hole left by ionisation and make more energy available to the photoelectron. In a more realistic scheme, the final state energy is equivalent to that of the ion. In this adiabatic approach, the atom is allowed to fully relax to its ionic configuration before the photoelectron is ejected. A consequence of relaxation is that the Koopmans state must be expanded as a linear combination of relaxed final states, allowing the appearance of final state satellite structure in the photoelectron spectrum^{2,5}.

2.2 Surface Sensitivity

Before emission into the vacuum, electrons of the energies experienced in electron spectroscopy may lose energy through a variety of quantised processes. Firstly, they may excite phonon vibrations within the bulk lattice. Phonons are the collective oscillations of atoms either at the surface or in the bulk. Such losses are of the order of a few tens of millielectronvolts and so are not generally resolved in a conventional spectrometer but will contribute to the unresolved low kinetic energy side of a typical photoelectron peak.

The dominant loss mechanism in metals is due to the excitation of plasmons^{2,6}; collective oscillations of the electron gas. Plasmon loss structure may be the result of intrinsic or extrinsic processes. If photoemission is considered as a three step model^{2,7}; (i) excitation (ii) transport of the electron to the solid surface and (iii) escape into the vacuum, losses can occur at any step. Step (i) produces the main photoelectron line if no losses due to (ii) and (iii) occur. Quantised losses incurred through steps (ii) and (iii) constitute excitation of bulk and surface plasmons respectively.

An electron of very low kinetic energy will be unable to excite the above processes and so its pathlength λ in the solid will be long. Above the

plasmon energy, the probability of sequential plasmon generated losses increases sharply and the electron free path reaches a minimum at approximately 2 or 3 times the plasma energy^{2.6}. At high kinetic energy the cross-section for the excitation of plasmons falls and again the pathlength is large. As a consequence, the surface sensitivity of many electron spectroscopic techniques is a function of the photoelectron kinetic energy. The most surface sensitive region (ie the shortest mean free path) occurs for electrons of roughly 30-100eV kinetic energy and the pathlength under these conditions is typically 5-10Å. The pathlength is material dependant and a broad scatter of experimentally determined pathlengths allows the plotting of the so-called 'universal curve' of surface sensitivity as shown in figure 2.1^{2.3, 2.8}. For electron kinetic energy $KE > 200\text{eV}$, the pathlength has been shown to be approximately proportional to $KE^{0.75}$ both theoretically^{2.9} and experimentally^{2.10}.

Surface sensitivity is therefore a reflection of the probability of an electron escaping to the surface without energy loss. The depth of radiation penetration in XPS and UPS exceeds the depth from which electrons can escape from within a solid to the surface. Surface sensitivity is thus largely independent of the energy of the incident radiation.

Emission of electrons from a solid can be stimulated by photon (photoemission) or electron beams. Three of the most common kinds of electron spectroscopy, discussed below, are illustrated diagrammatically in figure 2.2

2.3 X-ray Photoelectron Spectroscopy (XPS)

2.3.1 Primary Structure

X-ray photoelectron spectra are typically excited using Mg or Al $K\alpha_{1,2}$ radiation (an explanation of the notation used is given below). Impact by high energy electrons creates core holes in the 1s shell of the anode element leaving it ionised. Decay of a 1s hole state, $2p_{3/2}$ or $2p_{1/2} \rightarrow 1s$ can emit soft x-ray photons of 1253.6eV (Mg) or 1486.6eV (Al) (main intensity) as shown schematically in figure 2.3. The photon source output is usually unmonochromated and a broad energy spectrum due to Bremsstrahlung results, with the characteristic anode lines superimposed. The anode lines

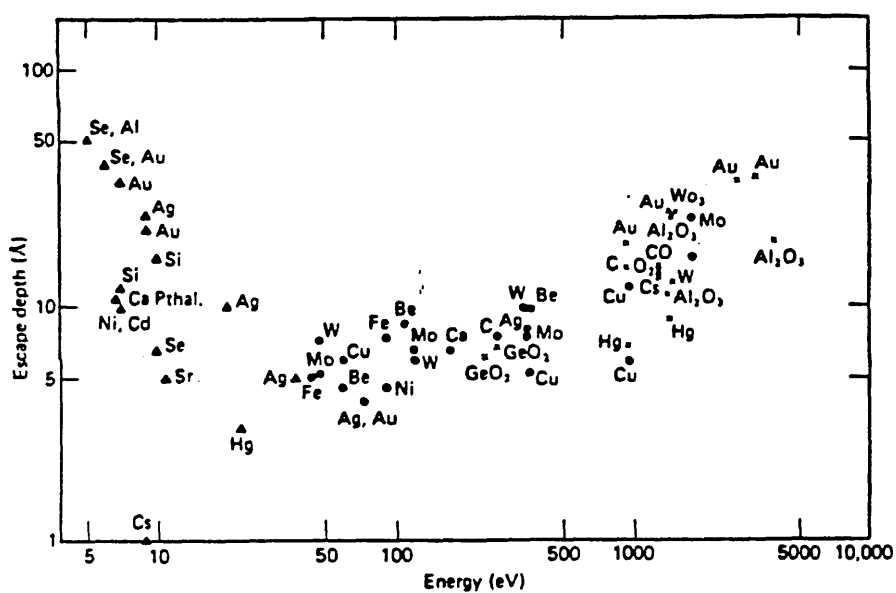


Figure 2.1: The 'universal curve' of electron escape depth for a particular kinetic energy^{2.3, 2.8}. The broad scatter of experimentally determined data points show similar behaviour and maximum surface sensitivity (minimum pathlength) is achieved by utilising electrons of $\approx 30\text{-}100\text{eV}$ kinetic energy.

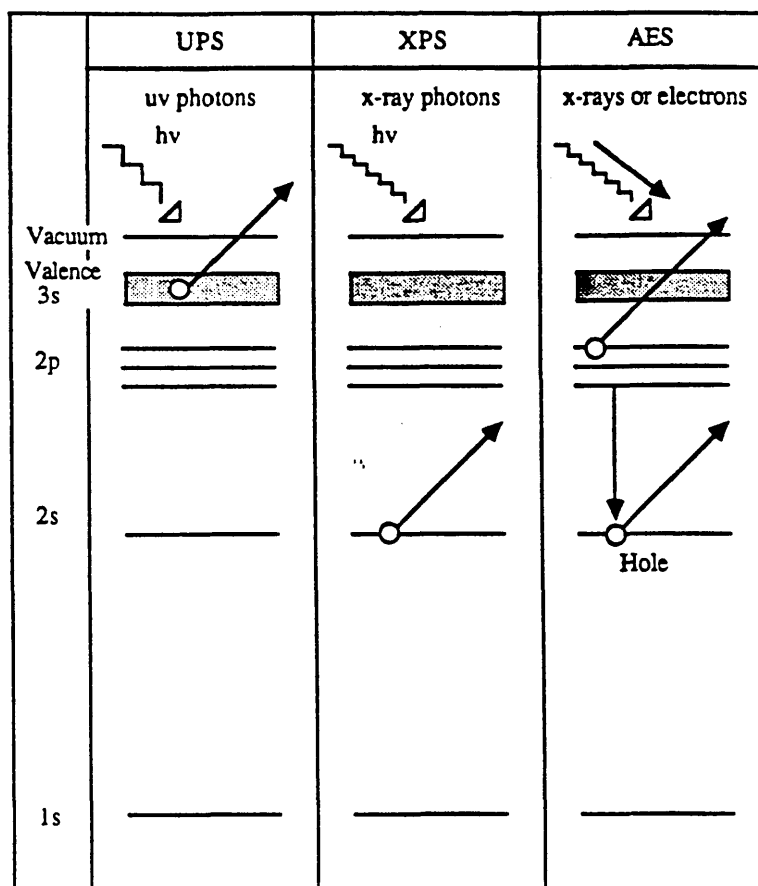


Figure 2.2: Three types of electron spectroscopy. In ultra-violet photoelectron spectroscopy (UPS), photons only have sufficient energy to eject valence electrons. Soft x-ray photons used in the x-ray photoelectron spectroscopy (XPS) technique can eject electrons from both core and valence levels. In Auger electron spectroscopy (AES), a core hole (O) produced by either electron or photon irradiation is filled by internal electron rearrangement resulting in the emission of a further electron to leave the atom doubly ionised.

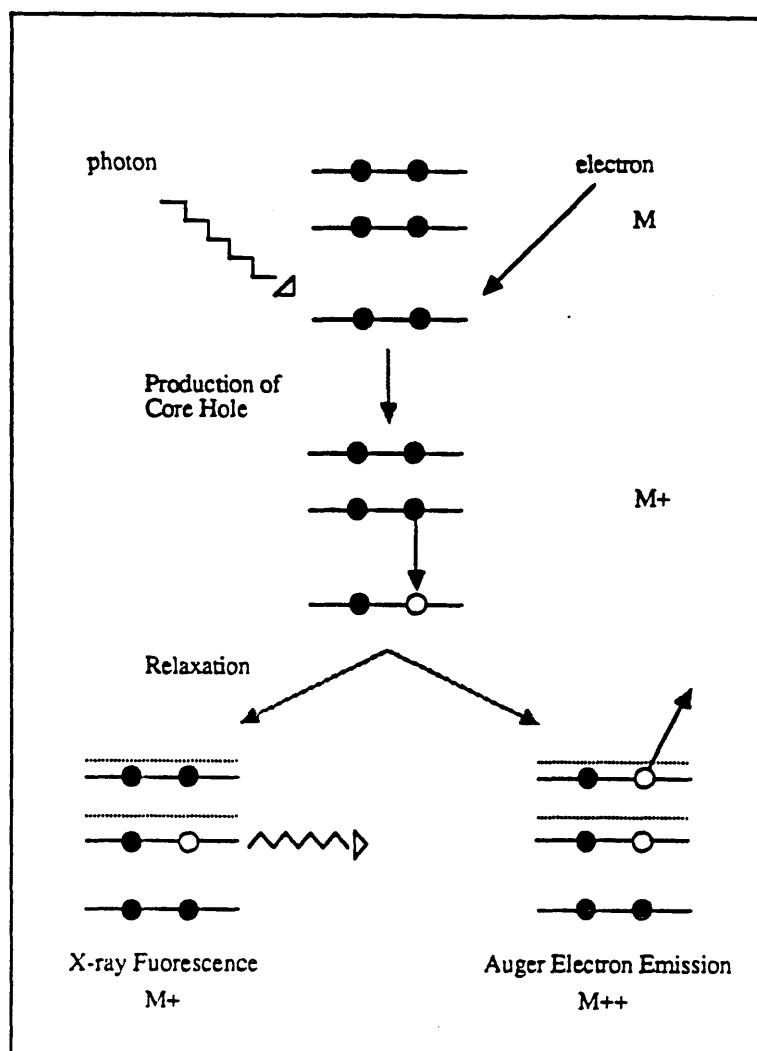


Figure 2.3: The decay of a core hole can occur *via* emission of an electron in a radiationless manner (the Auger electron) or by emission of a photon (x-ray fluorescence)^{2,3}. In the latter process, decay of a 1s hole state, $2p_{3/2}$ or $2p_{1/2} \rightarrow 1s$ ($K\alpha_{1,2}$) in a Mg or Al anode material emits x-ray photons of 1253.6 or 1486.6eV respectively. These photon energies are commonly used to excite x-ray photoelectron spectra.

have an intrinsic linewidth of $\approx 0.7\text{eV}$ (Mg) or 0.85eV (Al) which can be reduced to $\approx 0.2\text{eV}$ with monochromation^{2.11}.

See Erratta→

A typical XPS spectrum shows the photoelectron peaks characteristic of the sample, both valence and core levels, and peaks due to Auger electrons (see later). The combination of the broad Bremsstrahlung background together with the loss processes mentioned above cause these peaks to be superimposed upon a steeply rising background of secondary electrons. Steps in background intensity occur to the low binding energy side of a peak as the result of inelastically scattered electrons reaching the surface as illustrated by the typical XPS spectrum shown in figure 2.4. Close examination of this spectrum of Ti foil after annealing reveals that some of the photoelectron peaks are split into doublets (eg. Ti:2p) by a process termed multiplet splitting.

(i) Multiplet and Exchange Splitting

See Erratta→

If we consider the electron as a charged particle orbiting a nucleus, the electron possesses an associated angular momentum l which can take values 0, 1, 2, 3... This circulating current gives rise to a magnetic field. In addition, the electron possesses one of two possible spin orientations corresponding to m_s of $\pm 1/2$. The electron spin has an associated spin angular momentum s that can interact with the magnetic field due to angular momentum. The total electronic angular momentum j associated with the electron orbiting the nucleus is then the vector summation of the orbital angular momentum and the spin momentum $j = l + s$. For example, a 2p electron has $l=1$ and $s=\pm 1/2$ so j takes values of $1/2$ and $3/2$. The $2p_{1/2}$ level is lowest in energy reflecting the 'anti-parallel' nature of the vector addition. Obviously, s electrons possess no orbital angular momentum ($l = 0$) so no spin-orbit coupling occurs.

Since the individual j values for each electron are summed $j = l + s$. The total electronic angular momentum is then $= \sum j$ and this summation scheme is termed 'j-j' coupling.

The magnitude and direction of the momentum interaction (spin-orbit coupling) are determined by the nuclear charge of the atom, the electron

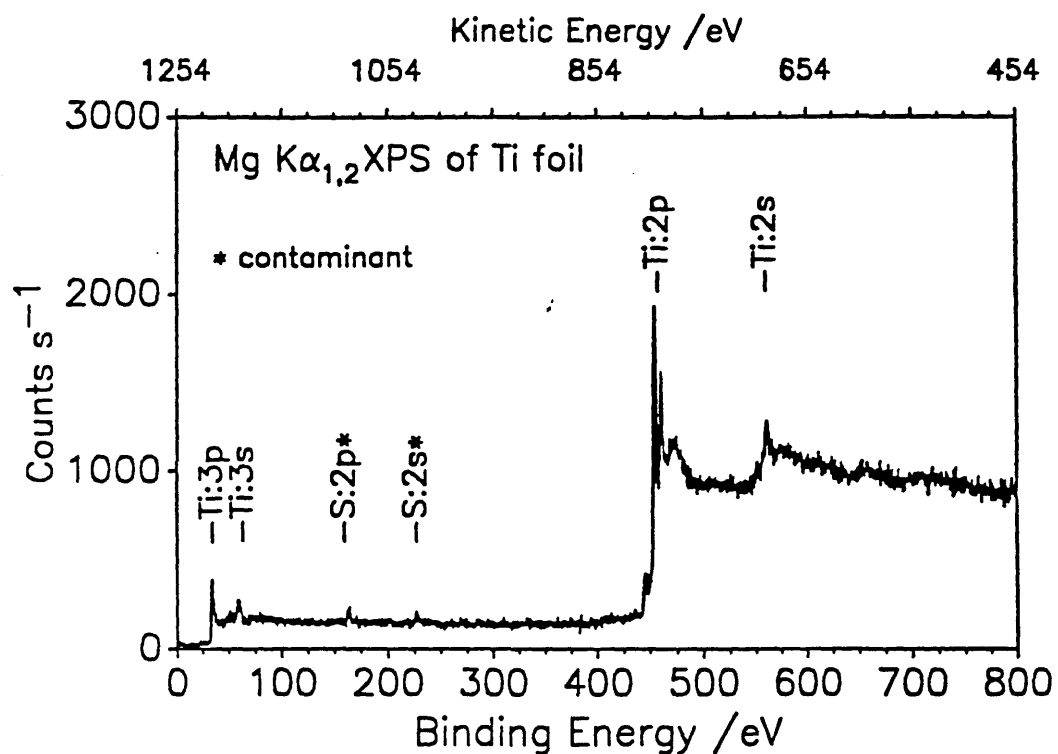
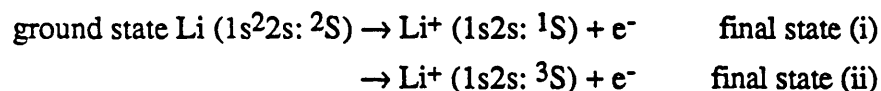


Figure 2.4: A typical XPS spectrum excited by Mg $K\alpha$ radiation. This single sweep spectrum shows peaks due to Ti core levels and some weak S contamination after heating in vacuum. Spin-orbit coupling and the presence of the $K\alpha_{3,4}$ x-ray satellite can be seen in the Ti:2p peak.

velocity and radius. For a particular primary quantum number n , the coupling depends on $1/r^3$ where r is the mean orbital radius. An electron orbiting a large nuclear charge (large Z) at a small mean radius (deep core level) will give rise to a large magnetic field and the spin-orbit interaction will thus be large. Conversely, a valence electron orbiting a smaller nuclear charge gives rise to much smaller coupling. As a consequence of spin-orbit coupling, the p, d, f photoelectron core lines ($l > 0$) are split into doublets. The relative intensities of the peaks in the doublet are given by the degeneracy, $2j + 1$. Hence, the $p_{1/2}$ and $p_{3/2}$ peaks are in the ratio 1:2, the $d_{3/2}$ and $d_{5/2}$ in the ratio 2:3.

Splitting may occasionally be observed in s level core peaks, where spin-orbit coupling is expected to be zero. Such structure is encountered in cases where photoemission occurs from a filled shell in the presence of an open one. For example, in the case of 1s emission from a Li atom, there are two possible final states,



(ii) Core Level Chemical Shifts

Non-equivalent atoms of the same element give rise to core level photoemission peaks of measurably different binding energy. Since the binding energy of an electron in a particular atom will be sensitive to any surrounding potential, atoms on different lattice sites, with different formal oxidation state or in a different chemical environment will produce photoelectron peaks characterised by different binding energies. In favourable circumstances, core level shifts can allow atoms of the top atomic layer to be distinguished from those in the lower layers. By reference to well characterised standard materials, information about the chemical environment of an atom can be gained.

Chemical shifts are of considerable practical importance in XPS and extensive tables of binding energies and chemical shifts have been prepared^{2,12}. Obviously, for absolute binding energy measurement the need for an accurately determined spectrometer reference is important. Common

standards include the Au:4f_{7/2} or the Ag:3d_{5/2} peak^{2.13}.

2.3.2 Fine Structure

(i) X-ray Satellites

Whilst the K $\alpha_{1,2}$ unresolved doublet is the most probable emission process in the x-ray source anode, the same transitions may occur in a doubly charged anode atom. These K $\alpha_{3,4}$ transitions are typically <10% as intense as the K $\alpha_{1,2}$ but 'ghost' peaks in the spectra are caused at about 10eV higher kinetic energy. K β transitions from the 3p_{3/2} and 3p_{1/2}→1s hole can also produce photons, with an intensity of about 1% of the K $\alpha_{1,2}$ as shown in table 2.1.

(ii) Shake-up, Shake-down and Shake-off

The sudden approximation is useful in explaining the presence of intrinsic loss features due so-called 'shake-up' satellites. As the ion is created during photoemission (but 'before' the photoelectron has left the vicinity of the atom!), remaining electrons experience an apparent increase in the effective nuclear charge. The resulting relaxation can lead to the promotion of a valence electron to a higher bound unoccupied orbital. The energy required to promote is then unavailable to the photoelectron and so a 'shake-up' satellite peak appears to *lower* kinetic energy of the primary photoelectron structure. Alternatively, the core hole may pull a previously empty level below occupied levels: this two hole satellite peak then appears to *higher* electron kinetic energy as a 'shake-down' satellite.

If electron promotion occurs to an unbound state (ie to the continuum), the process is termed 'shake-off' and leaves a hole in both core and valence levels. Although it is convenient to explain intrinsic loss features such as shake-up and shake-off in terms of sudden and adiabatic approximations, strictly they are many electron processes synchronous with the primary photoionisation event.

Table 2.1: X-ray satellites of twin anode materials^{2,7}

		Photon energy (h ν) /eV	Intensity %
Mg	K $\alpha_{1,2}$	1253.6	100
	K α_3	1262.1	9
	K α_4	1263.7	5
Al	K $\alpha_{1,2}$	1486.6	100
	K α_3	1496.3	7
	K α_4	1498.3	3

(iii) Electron-Hole Excitations

In a metal, a continuous spectrum of electron-hole pair excitations of very small energy ($<1\text{eV}$) can occur as the result of electron promotion from the valence levels to a series of unoccupied one-electron bound states (near continuum) just above the Fermi level^{2.14, 2.15}. This energy is then unavailable to the primary photoelectron. Of lower energy than usual shake-up satellites, rather than produce discrete structure, these losses cause an asymmetry to the low kinetic energy side of the photoelectron peak. The effect is proportional to the density of electron states (DOS) at E_F .

2.4 The Probability of Interaction: Ionisation Cross-section

The probability of core-hole generation is given by the photoelectron ionisation cross-section σ . The cross-section is a function of the initial state wavefunction and final state wavefunctions of the photoelectron. The transition probability between these two states is determined by an operator r_μ . So the cross-section for photoionisation of a system in initial state i by a photon of energy $h\nu$ to a final state j (which is the photoelectron of energy ϵ and an ion) can be written as^{2.16},

$$\sigma_{ij}(\epsilon) = A | \langle \psi_i | r_\mu | \psi_j \rangle |^2 \quad (2.3)$$

where A is a constant dependent on the photoelectron energy ϵ and I_{ij} the ionisation potential ($E_B + \phi$). The term $\langle \psi_i | r_\mu | \psi_j \rangle$ is called the dipole matrix element. Tables have been prepared for σ as determined both experimentally^{2.17, 2.18} and theoretically^{2.19}.

2.5 Effect of Take-off Angle in XPS

The attenuation of electron intensity with depth into a sample is given by^{2.20},

$$I = I_0 \exp (-d/\lambda \cos\alpha) \quad (2.4)$$

and so the effective sampling depth is,

$$d = \ln(I_0 / I) \lambda \cos \alpha \quad (2.5)$$

where I is the measured intensity of photoelectrons emerging from a depth d , α is the angle of measurement from the surface normal and λ is the electron mean free pathlength. It can be seen from (2.5) that 95% of the sample intensity originates within 3λ of the surface and the sampled depth d is greatest when $\alpha = 0^\circ$ (ie normal to the surface). If measurement is performed away from the surface normal, the effective depth sampled is reduced. In this way, by altering the measured photoelectron 'take-off' angle, the effective sampling depth can be reduced. For example, when $\alpha = 75^\circ$, d is reduced to approximately one quarter of the normal value.

2.6 Ultra-violet Photoelectron Spectroscopy (UPS)

As an alternative to x-ray excitation, ultra-violet radiation may be used to generate photoelectrons. Photons of this relatively low kinetic energy are able to eject the most weakly bound electrons only; the valence shells. The most common photons used in UPS are those from the $2p^1 1s^1 \rightarrow 1s^2$ transition in excited Helium atoms at 21.2eV (He (I) α). The gas discharge lamp can also be operated to maximise the $2p^1 1s^0 \rightarrow 1s^1$ transition in the He⁺ ion giving photons of 40.8eV (He (II) α). Features due to He (II) are seen in He (I) spectra with approximately $1/10$ the intensity. Typical linewidths are a few millivolts.

Since it is the valence levels of a sample that are involved in chemical bonding, the bonding orbitals of adsorbed molecules are accessible with UPS. As a consequence, UPS has been used to elucidate both the band structure of clean surfaces and the adsorption behaviour of molecules upon clean surfaces. On a clean polycrystalline metal surface, the UPS spectrum will roughly mirror the occupied density of states (DOS). This will be represented as broad peaks superimposed upon a sharply rising background due to inelastically scattered secondary electrons. This drops quickly to zero intensity at a photoelectron binding energy of $E_{\text{photon}} - \phi$ where E_{photon} is the photon energy and ϕ the sample workfunction.

2.7 Auger Electron Spectroscopy (AES)

As mentioned previously, when a core hole is created it can be destroyed by an electron from a shallow level filling it. Dissipation of excess energy is by emission of either an x-ray photon or another electron from a shallower level in a radiationless manner. The ion is left doubly charged. It is obvious that this process is not dependent on the incident energy, but is intrinsic to the element. This Auger electron, as measured in Auger electron spectroscopy (AES), can also be used to interpret the chemical state and environment of the atom in a similar way to XPS.

The energy of the Auger electron is approximated by^{2,20},

$$E_k \approx E_{\text{core}} - E_1 - E_2 - \phi \quad (2.6)$$

where E_1 and E_2 are the binding energies of two shallow levels. A simple diagram of this process is shown in figure 2.5. The energy is only approximated in the above expression since the effects of final state hole-hole coupling exactly determine E_k (whether the holes are located in core or valence sites). X-ray notation is used to describe the transition, for example, $KL_{2,3}L_{2,3}$ means a core hole created in the K shell is destroyed by a $L_{2,3}$ (2p) electron together with emission of another $L_{2,3}$ electron (the Auger electron). The letter V is used in transitions involving valence electrons eg. $L_{2,3}VV$.

Auger electrons are produced with the same range of energies as photoelectrons and so are of similar surface sensitivity. Whilst Auger electrons can be produced by photons or electrons, the ease and low cost of producing electron sources make electron excited Auger spectra more commonly encountered. Moreover, electron beams can be easily focussed to sub- μ sizes for excellent spatial resolution, or they can be rastered over an area for information on inhomogeneous surfaces. Scanning Auger systems are therefore much easier to manufacture than scanning XPS instruments although the latter have been recently developed^{2,21}.

A typical electron excited Auger spectrum shows Auger peaks superimposed upon a very strong, steeply rising background produced by inelastic scattering as discussed previously. Inelastic contributions are

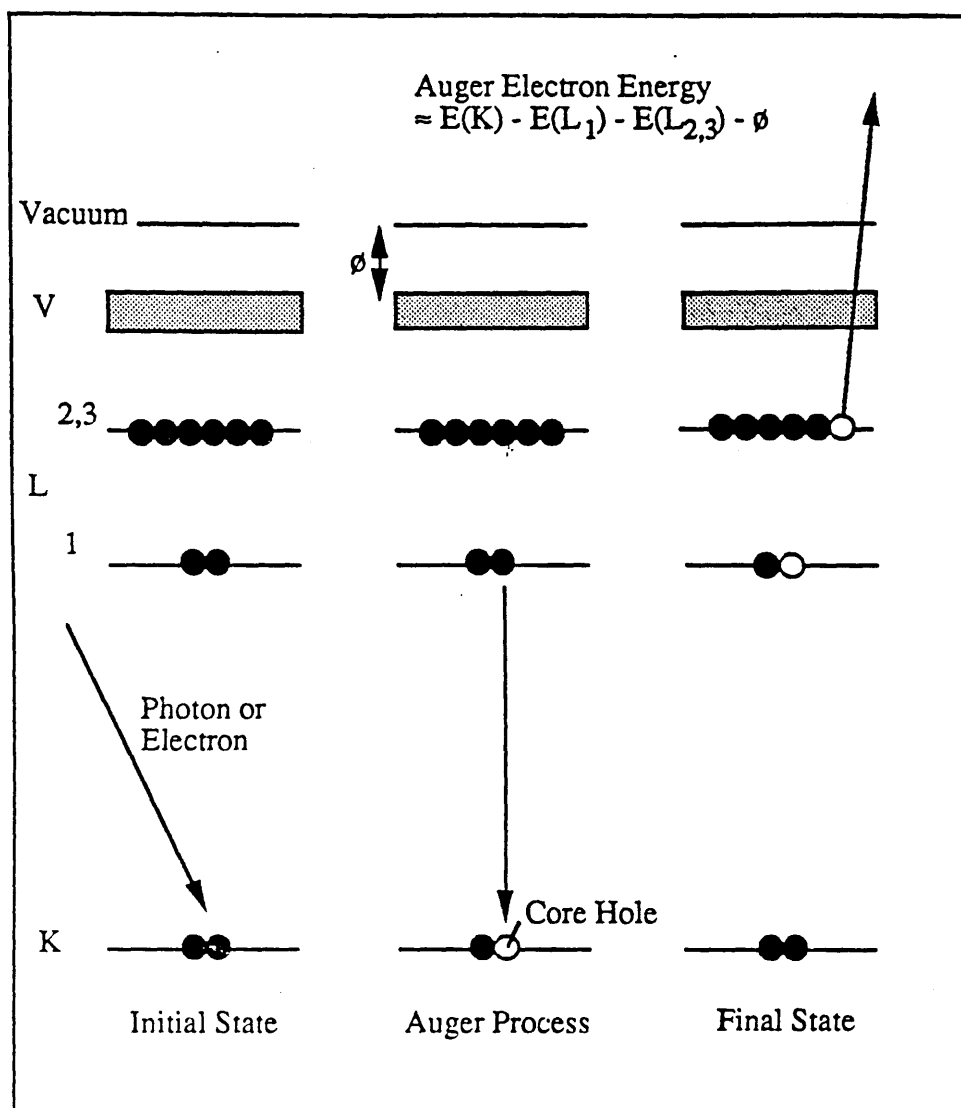


Figure 2.5: Diagram illustrating the Auger process. A core hole in the K shell ($1s$) of the atom, is filled by an L_1 ($2s$) electron, resulting in the synchronous release of a $L_{2,3}$ ($2p$) electron (the $KL_1L_{2,3}$ Auger electron). This electron has a kinetic energy independent of the incident radiation. The energy levels are stabilised by relaxation.

greater than in XPS, reflecting the the fact that secondary electrons from underlying atoms plus scattered electrons from the source are involved. Often, spectra are represented as the first derivative (dN/dE or $N'(E)$), allowing peak positions to be more accurately analysed than in the usual integral ($N(E)$) spectra.

Although the Auger process involves three electron transitions making it inherently more complex and difficult to interpret, it does show similar effects to those seen in XPS: chemical shifts, relaxations and loss features. Transitions involving valence levels can be particularly useful since they are relatively intense (a consequence of the relatively high density of electrons in the valence bands compared to core levels) and are involved in bonding (for example, to adsorbates).

2.8 Low Energy Electron Diffraction (LEED)

All the techniques discussed so far are sensitive to surface chemical composition. In contrast, the technique of low energy electron diffraction is sensitive to surface structure.

Electrons are much more strongly scattered than either x-rays or neutrons and are back-scattered at energies below about $1000\text{eV}^{2.8}$. Hence, electrons with de Broglie wavelength similar to atomic spacings will be scattered from a solid crystalline surface making them suitable for diffraction purposes. In the usual LEED apparatus, electrons are directed along the surface normal and are backscattered by the surface. The electrons may interfere and those constructively reinforced are captured by a semi-spherical phosphor screen and displayed as a regular array of bright spots. The diffraction pattern approximately represents the two dimensional reciprocal lattice of the surface.

The de Broglie wavelength of a wave-particle is given by^{2.22}

$$\lambda = h/p \quad \text{or} \quad h/\sqrt{2m_e V} \quad (2.7)$$

where an electron of mass m_e has momentum p and V is the electron energy in electronvolts. Hence, electrons with energy of about $20\text{-}200\text{eV}$ have

wavelengths of atomic dimensions and in addition possess the previously discussed surface sensitivity. For a diffraction pattern spot to be produced at an angle θ from the surface normal, the Bragg condition,

See Erratta→

$$n\lambda = 2d \sin\theta \quad (2.8)$$

for constructive interference from a lattice spacing d , must be satisfied. By measuring the angle θ at the screen, the row spacing giving rise to the spot can be calculated. In this way, diffraction spots can be labelled with the appropriate Miller indices causing the scattering. LEED is a very powerful technique, especially if combined with other techniques sensitive to surface composition, and in addition to providing information about the atomic spacings of a clean surface, adsorbates ordering in a regular way (one or two dimensions) will also give rise to a characteristic diffraction pattern^{2.23}.

2.9 Electron Energy Loss Spectroscopy (EELS and HREELS)

Electron energy loss spectroscopy (EELS) can be used to examine both the electronic and vibrational excitations of a solid. Initially, the technique was used to study bulk excitations by transmission of high energy electron beams (5-50keV) through very thin samples such as those prepared for an electron microscope. However, the last decade has seen effort directed towards the design of a high resolution spectrometer using low energy electrons (<1000eV), scattering the beam from a flat sample.

Advances in engineering and electron optics have allowed the development of highly monochromated electron sources with beam widths of a few millielectronvolts. This has resulted in a rapid expansion of the field of high resolution electron energy loss spectroscopy (HREELS) using beam energies of typically 5-10eV. Such an experimental technique has become a very powerful tool for the analysis of the vibrations of adsorbed molecules. In HREELS, the electron can no longer be considered as penetrating the surface at all, but is scattered at or near the surface by a variety of processes. The most important mechanisms relevant to the present work are termed dipole scattering and impact scattering and are introduced below.

2.9.1 An Introduction to Dipole Scattering

In dipole scattering, the incoming electron interacts with the long range intrinsic time-dependent dipole moment of the surface or that induced by a layer of an adsorbed species^{2,24}. The intrinsic surface static dipole moment is modulated by the adsorbate moment μ and an oscillating electric field is created extending above the solid and decaying as $1/r^3$ with distance from the surface r . The presence of a dipole above the surface creates an image dipole in the substrate. When the molecular dipole is arranged perpendicular to the surface plane the total dipole moment becomes $2\mu_{\perp}$. However, if the dipole is oriented parallel with the surface plane, the image dipole is oriented antiparallel to it, and tends to cancel out the electric field set up by the real dipole. Thus the effective dipole moment vanishes.

$$\mu_{||} = -\mu_{||} \text{ (image)}$$

$$\mu_{\perp} = \mu_{\perp} \text{ (image)}$$

$$\text{so } \mu_{\perp}^{\text{total}} \text{ tends to } 2\mu_{\perp}$$

$$\text{and } \mu_{||}^{\text{total}} \text{ tends to zero}$$

(2.9)

This is an important result and leads to the idea that when long range dipole interaction is the scattering mechanism, only vibrational modes excited perpendicular to the surface will be visible. This is in effect the 'dipole scattering selection rule'.

If there is no interaction between an adsorbed atom and incoming electron, there will be no momentum transfer to the surface and the incident and reflected beam angles will be equal. Hence, the elastic beam is strongly scattered in the specular direction.

The surface layer, whether it is an ordered clean metal face or the regular arrangement of adsorbate molecules, can be excited in the direction perpendicular to the surface plane. The long range nature of the dipolar interaction means that individual atoms at the surface cannot be excited (the electron cannot distinguish individual dipoles at such a distance, only the overall electric field). Hence the layer vibrates collectively in the delocalised manner constituting the creation of a surface phonon.

2.9.2 Dipole Theory of One-phonon Excitation

A surface optical phonon is a two dimensional collective oscillation of the outermost atomic layers of a solid. An 'optical' phonon is created by individual atomic vibrations within a unit cell and is of appropriate wavelength to interact with electromagnetic radiation^{2.22}. The adsorbate layer is treated as an infinite array of point charges located at a small distance above the dipole image plane (the surface)^{2.25}. The amplitude decays exponentially with depth into the bulk and propagates along surface with a characteristic wavelength λ . The parallel momentum associated with the phonon mode is related to the wavelength by $|q_{||}| = 2\pi / \lambda$. As can be seen, small wavelengths imply a large momentum (in effect, small λ means excitation of single surface bond). Large phonon wavelengths imply a small associated momentum, as is the case of the dipole scattering in HREELS. So although only the perpendicular vibration of each surface atom or molecule is excited in dipole scattering, incident electron beam momentum is transferred parallel to the surface as surface phonon oscillations.

If the incoming electron does excite vibration in the adsorbate, momentum is lost to the surface phonon and the surface parallel component of the outgoing electron momentum will be reduced after reflection. If one considers the electron approaching the surface with incident energy E_i and wavevector $\mathbf{k}^i$ then the inelastically scattered electron will have energy E_s and wavevector $\mathbf{k}^s$ such that,

$$\begin{aligned} E_s &= E_i - \hbar\omega \\ \mathbf{k}^s_{||} &= \mathbf{k}^i_{||} - \mathbf{q}_{||} \end{aligned} \tag{2.10}$$

where $\mathbf{q}_{||}$ is the momentum transfer to the excitation by conservation of system total momentum. The energy lost to the surface phonon is $\hbar\omega$ ($=\hbar\nu$).

The momentum transfer to the surface relative to the incident beam momentum is typically very small (ie $\mathbf{q}_{||} = \mathbf{k}^i_{||} - \mathbf{k}^s_{||}$ is small). By reference to figure 2.6, it can be seen that if the incident and scattered electron momentum is resolved into respective parallel and perpendicular components, the scattered beam direction is away from the specular direction

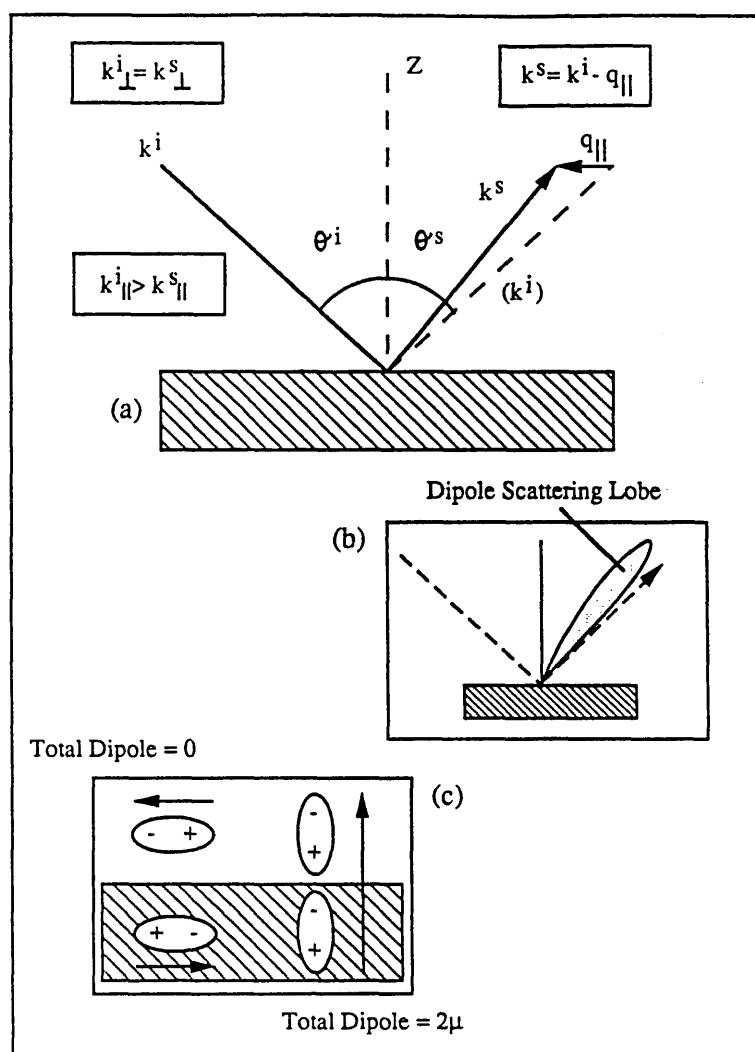


Figure 2.6: Diagrammatic representation of the dipole scattering mechanism in HREELS. (a) The incident electron is scattered from the surface after excitation of a surface phonon. Momentum is transferred to the surface phonon q in such a way that a small component of initial electron momentum parallel to the surface plane $k_{||}^i$ is reduced by $q_{||}$. The scattered electron has reduced parallel momentum ($k_{||}^i > k_{||}^s$, $k_{||}^i = k_{||}^s + q_{||}$). Perpendicular momentum is conserved ($k_{\perp}^i = k_{\perp}^s$). (b) As a consequence, inelastically scattered electron intensity is directed into a 'dipole scattering lobe', which is shifted closer to the surface normal than the elastically scattered beam. (c) Illustration of the 'dipole selection rule'. A molecular dipole μ aligned perpendicular to the surface plane creates an image dipole at the same distance below the surface. The total dipole then $\rightarrow 2\mu$. However, if the dipole of an adsorbed molecule is aligned parallel to the surface plane, the total dipole $\rightarrow 0$.

and toward the surface normal. In addition, this pronounced degree of forward scattering is accentuated with increasing loss energy creating a narrow 'dipole lobe' of inelastically scattered electrons.

In scattering events where there is a large momentum transfer to the adsorbate, as in 'impact scattering', the incoming electron effectively interacts with the short range atomic potentials of a single adsorbate species. In this case, the incident beam can excite either perpendicular vibration (metal-adsorbate 'stretches') or parallel vibrational modes ('wagging' or 'bending') and the scattered electrons emerge with a broad angular distribution.

Whilst both scattering processes will occur at a real surface, the dipole scattering mechanism dominates in the near-specular direction. Moving the electron energy analyser of the HREELS system away from the dipole lobe allows the experimentalist to separate the metal-adsorbate stretches visible in the near-specular direction as the result of dipole scattering from bending modes excited off-specularly by the impact mechanism.

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3. Experimental Methods: Vacuum System Design and Sample Treatment

3.1 The Importance of Ultra-High Vacuum

The use of surface specific electron spectroscopies imposes constraints on the design of a spectrometer. Firstly, it is essential for photoelectrons to reach the detector having suffered the minimum number of collisions with intervening gas atoms. If we assume a typical vacuum chamber with a sample to detector distance of 1m, then the mean free path of the electron in the vacuum should be at least of this order. In this respect, pressures of below 10^{-6} torr are necessary^{3.1}.

Secondly, many clean metal surfaces react rapidly at ambient pressure with atmospheric gases and the surface investigated is changed radically. The kinetic theory of gases allows the calculation of the number of gas particles impinging on a surface Z_{surface} at a given pressure in a given length of time^{3.1}.

$$Z_{\text{surface}} = P (1 / 2\pi k_B T m)^{1/2} \quad (3.1)$$

where P is pressure, k_B is the Boltzmann constant and m the particle mass. If P is measured in torr and m is substituted for M , the molecular weight of the gas molecules, Z_{surface} can be rewritten as

$$Z_{\text{surface}} = 3.51 \times 10^{22} P / (TM)^{1/2} \quad (3.2)$$

If the concentration of surface atoms is estimated to be $3 \times 10^{15} \text{cm}^{-2}$, at a pressure of 1 torr and a sticking probability of unity, a monolayer of N_2 molecules will cover a surface in about 10^{-5} s. At 10^{-9} torr, a monolayer is formed in about 10^4 s or 2.5 hours. This imposes a much greater demand on the vacuum conditions, and only at pressures of 10^{-10} torr or below is the flux of molecules striking a surface sufficiently low to allow experimentation in a reasonable length of time^{3.2}.

3.2 General Spectrometer Features and Construction

A typical vacuum chamber^{3.3} is made of welded stainless steel throughout to provide low outgassing and corrosion rates. At atmosphere, gas molecules can adsorb onto the inner walls of the chamber. These molecules are removed only slowly by the vacuum pumps, and so the whole system is designed to be heated to a few hundred degrees Celcius to facilitate rapid desorption of these molecules whilst the system is pumped. Additionally, all internal fabrication is with low vapour pressure materials such as 316 stainless steel, μ -metal, Cu, Ta, Mo and ceramics such as alumina and silica.

An electron spectrometer also features a means of exciting spectra, whether by electrons, photons, atoms or ions, together with an appropriate detector/counter. Some sort of UHV pressure gauge for use in dosing experiments and for monitoring vacuum performance is usual. There is often a means to move the sample inside the chamber, especially in multi-technique machines, and most manipulators include facilities for sample heating and/or cooling and for altering the sample orientation. Often, specific preparation equipment such as heaters, evaporators, cleavers, ion etchers or high-pressure cells are dedicated to the requirements of a particular sample and instrument. Although spectrometers vary widely in their individual design, the same major constructional features are employed throughout. With careful use, a modern ultra-high vacuum system can easily attain pressures of 10^{-10} torr. A simple schematic of a UHV spectrometer equipped with both an x-ray source and electron source is shown in figure 3.1.

3.3 Excitation

Soft x-ray sources with photon energies of 1 to 2keV are the most commonly encountered photon sources and have the advantage that they can be used to eject both core and valence electrons. In contrast, ultra-violet radiation only has sufficient energy to displace the most weakly bound (valence) shells of most atoms. Obviously, it would be advantageous to use a single high-intensity photon source of continuously variable photon wavelength between these two extremes. Such specifications are not easily met. However the tangentially emitted photon flux from an electron beam

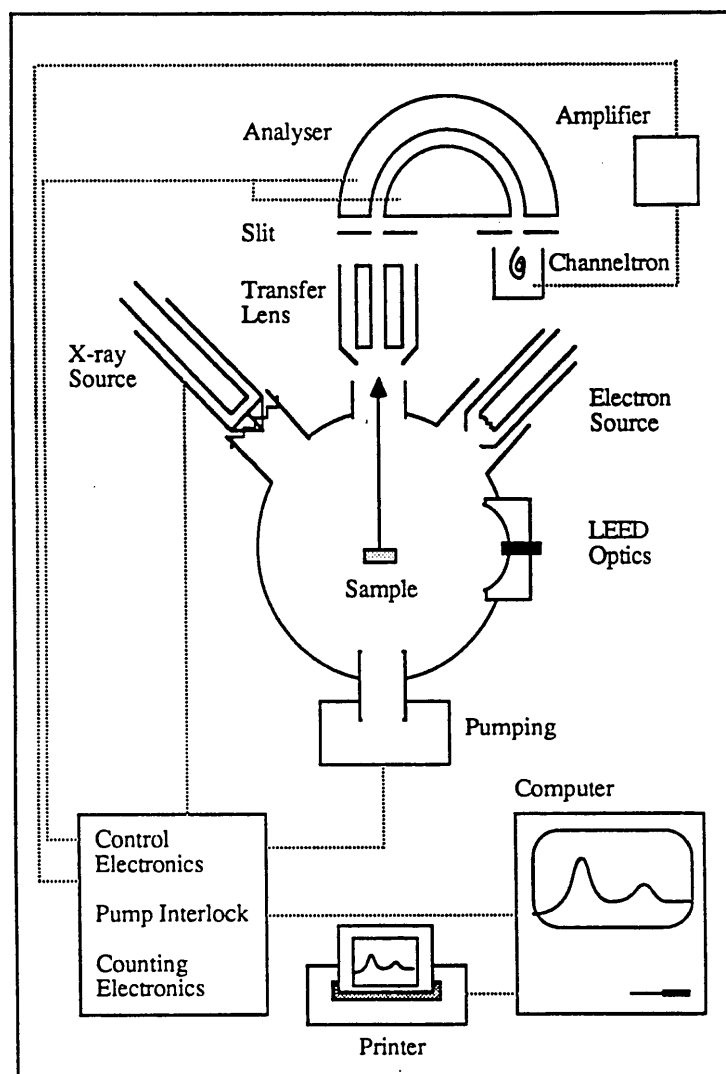


Figure 3.1: Schematic of a simple ultra-high vacuum chamber equipped with a hemispherical analyser, an x-ray source for XPS, an electron gun for AES and EELS and LEED optics for surface structure determination.

storage ring, once suitably monochromated, is an excellent way to excite photoelectron spectra, and indeed extensive research is performed on these 'synchrotron' sources^{3,4}. Such highly specialised instruments are usually owned on a national level.

3.3.1 X-ray Sources

Soft x-rays may be produced by bombardment of a metal target by high energy electrons. Such x-ray guns usually contain two metal anodes incorporated in the same housing. One is usually of Al and generates x-rays of 1486.6eV (main intensity), the other half is coated with Mg which produces 1253.6eV photons as discussed in chapter 2. The anode is water cooled to prevent vapourisation of the thin anode coatings ($\approx 10\mu\text{m}$) and is separated from the vacuum chamber by a thin Al window. The anode is held at a potential of +10 to +15kV relative to an associated filament which encircles it. When the filament is heated, electrons are produced by thermionic emission and accelerated toward the anode material. Core holes are produced in the anode atoms and these decay by electronic rearrangements within the atom resulting in the release of high intensity x-ray photons.

3.3.2 Ultra-violet Photon Sources

Emission lines from the decay of ionised gas atoms may be used to excite ultra-violet (UV) photoelectron spectra. The lamp consists of a discharge or excitation chamber, where a potential of a few kV will produce spontaneous ionisation of many noble gas atoms. A gun typically operates at $2\text{--}6 \times 10^{-6}$ torr chamber pressure. The most common gas discharge uses helium to give intense emission lines (He I = 21.21eV and He II = 40.8eV).

Since weakly bound valence electrons are probed by UV radiation, these photons interact strongly with many materials and the problem of including a suitable window to the chamber must be overcome. This is effected in most systems by operating with a *windowless* lamp. The lamp comprises three chambers with small connecting apertures to allow the radiation to escape. The gas pressure within the discharge chamber is relatively large and He is only allowed to escape into the next chamber

through the small aperture. This next chamber is pumped to about 10^{-3} torr and helium escaping into the third chamber is pumped by UHV pump.

3.4 Electron Sources

Electron guns are arguably the most common excitation source employed in a modern ultra-high vacuum spectrometer. The design of the gun varies widely but almost all rely on the thermionic emission of electrons from a filament surface at high temperatures followed by an electrostatic acceleration stage and a focussing/deflection stage. The thermal spread of the electrons obeys a Boltzmann distribution, increasing the linewidth at high temperature. Often the filament is treated to reduce the electron exit work function and thus produce emission at lower temperatures and materials such as thoria (ThO_2) coated iridium are preferred to uncoated tungsten owing to the lower work function of the former.

3.5 Electron Energy Analysers

3.5.1 Hemispherical Designs

Ubiquitous throughout photoelectron spectroscopy, the concentric hemispherical analyser (CHA) is used in both XPS, UPS and AES. Such an instrument is based on the deflection of electrons electrostatically. Simple electrostatic analysers consist of two concentric hemispheres, arranged so there is a continuous small gap between. Slits are added at the entrance and exit points. When used in conjunction with a suitable lens system, the slit size usually defines the sample area from which photoelectrons are collected. A voltage is applied so that the outer hemisphere is at a higher negative potential than the inner and electrons of a particular energy (the pass energy E_0) can pass and follow a central path between the two hemispheres to be counted at a suitable detector. By changing the potentials applied to each hemisphere in a controlled way, a moveable energy window can be swept over the photoelectron spectrum.

In addition to the energy spread of the photoelectrons passing the entrance slit, there is also an angular variation of the electron trajectories. The CHA focuses electrons of the same energy but of slightly different initial angular paths (typically angular acceptance is $1-6^\circ$) at the exit aperture. For a

complete hemisphere pair, first order focussing in two dimensions is achieved at 180°.

3.5.2 Resolution

The angular acceptance of the analyser and the pass energy largely determine the analyser performance. The energy resolution is limited by the electron pathlength in the analysing field and so the physical dimensions of the analyser are also important. The resolution ΔE for a particular electron energy E_0 is given approximately by^{3.5},

$$\frac{\Delta E}{E_0} = \frac{s}{2R_0} \quad (3.3)$$

where s is the slit width, R_0 is the radius of the central path through the hemispheres and E_0 is the pass energy. An electron which possesses the pass energy E_0 will, if entering the analyser without an angular deviation from the normal, follow a middle path between the two hemispheres. It can be seen from (3.3) that for given analyser dimensions, if the pass energy is lowered, ΔE is proportionately reduced; that is, resolution is increased.

Constant energy transmission is achieved by pre-retarding the incoming electrons to a fixed pass energy E_0 . In modern spectrometers an electron lens is incorporated before the retard grid to increase collection efficiency. The electrons of energy E entering the lens are measured at the counting device. The relation between E and E_0 is simply

$$E = R + E_0 + \phi \quad (3.4)$$

where R is the applied retard voltage and ϕ the analyser work function.

The experimental resolution is a convolution of the source linewidth ΔE_p , the analyser resolution ΔE_a and the intrinsic linewidth of the process generating the photoelectron ΔE_n . Assuming gaussian lineshapes^{3.5},

$$\Delta E = (\Delta E_n^2 + \Delta E_a^2 + \Delta E_p^2)^{1/2} \quad (3.5)$$

The analyser resolution ΔE_a may or may not be an major component of the total resolution depending on the experimental technique and so the analyser can be made to operate in one of two modes.

In the constant analyser energy mode mentioned above, it is the retard potential which scans a constant resolution window over the spectrum. By retarding electrons from their initial high energies to the lower pass energy value, immediate gains in resolution are achieved according to (3.3). Constant analyser energy (CAE) is often used in XPS, so that the contribution of the analyser resolution relative to the source linewidth can be made small for all initial electron kinetic energies.

It can be seen if the photoelectron kinetic energy is initially small, the amount of retardation necessary to reach a certain pass energy becomes proportionately less. Hence, the gain in resolution over an analyser without any retardation is decreased. In AES, the linewidth of the incident electron source is irrelevant. Since the ejected electron linewidth is inherent to the Auger process, and is typically 2-3eV wide, spectra are often recorded in the constant retard ratio (CRR) mode. Electrons are retarded to a certain *fraction* of their initial kinetic energy so that at low electron energies, resolution is high but transmission low. At high kinetic energies resolution is poorer but with higher sensitivity. This mode of operation helps to suppress the high secondary electron background characteristic of electron beam excited Auger spectra.

3.5.3 Cylindrical Sector Designs

In common with the 180° CHA mentioned above, the cylindrical sector analyser relies on electrostatic deflection. It is suited to 'ribbon shaped' electron beams^{3.6} since it offers strong first order focussing in one dimension at $\pi/\sqrt{2}$ (127.17°). This type of analyser is common in high resolution electron energy loss spectrometers designed to measure vibrational loss spectra with the highest possible resolution.

The requirement of high resolution necessitates the use of an analyser that will operate at very low pass energies. At these very low pass energies, stray surface potentials may accumulate on both the inner surfaces of the

analyser and the sample. Nonetheless, with careful optimisation of analyser design, pass energies of $\approx 0.1\text{eV}$ are possible and vibrational linewidths of below 1meV have been measured^{3,7}.

A source of resolution degradation often considered important in HREEL spectrometers occurs as the result of space-charge effects within the electron beam^{3,6}. The confinement of the intense electron beam along the length of the monochromator produces strong divergent forces, increasing the angular spread of the beam and introducing spatial aberration. Obviously these effects increase with the density of the beam, and the spectrometer will become 'monochromator limited' as the current through the sectors is increased. Samples with an uneven surface can also increase the angular distribution of the reflected electron beam. For this reason, HREELS is best suited to flat single-crystal surfaces. Fringing field effects are experienced at the edges of the cylindrical sectors and especially at the entrance and exit slits where the near-uniform field between the sectors terminates, again introducing resolution degradation.

3.5.4 Retarding Field Analysers

The requirements of an electron collection device used for simple LEED work are very different to those presented by the CHA. Retarding field analysers (RFA) are fitted as part of LEED optics. The retarding field analyser consists of a series of retard grids arranged concentrically some 15-25cm from the sample. The exciting electron gun is located at the centre of the grids and diffracted electrons from the surface pass through the grids. The grid potentials are set to filter out electrons that have been inelastically scattered at the surface. After the final grid, the coherently scattered electrons are accelerated to a detector, commonly, a simple phosphor screen. LEED patterns are then photographed through a conveniently placed viewport.

3.6 The Vacuum Generators ESCALAB System

3.6.1 Introduction

The Vacuum Generators ESCALAB used in the work presented here is a two chamber UHV unit with a separate sample fast entry lock for

convenient sample changing as shown in figure 3.2. The 300mm diameter analysis chamber is pumped by an ion pump assembly and a diffusion pump backed by a rotary pump. The chamber is also fitted with a three filament titanium sublimation pump. This chamber has a base pressure of approximately 5×10^{-11} mbar after a suitable baking procedure. This probably constitutes the ion gauge x-ray limit. The analysis chamber is separated from the preparation chamber by a large diameter gate valve. This chamber is pumped by another diffusion and rotary pump combination and is also fitted with a similar titanium sublimation facility. A further gate valve separates the fast entry lock, which is individually pumped by a rotary unit.

Samples can be moved inside the spectrometer by means of a sample transfer mechanism inside the preparation chamber. Samples are mounted on small metal stubs as shown in inset in figure 3.2, which can be transferred from fast entry lock to the preparation chamber and then to a manipulator in the analysis chamber by this mechanism.

3.6.2 Surface Analysis Facilities

The analysis chamber of the ESCALAB is fitted with a variety of surface analytical facilities. In addition to a twin anode Mg/Al 200W x-ray source for XPS, there is a windowless gas discharge lamp and its associated differential pumping for the excitation of spectra by a noble gas emission line (UPS). An electron gun which operates at between about 250eV and 5keV is included for Auger electron spectroscopy and electronic electron energy loss spectroscopy. The high precision manipulator allows sample translation in three dimensions plus full 360° rotation. The radiation sources approximately converge at one position in the chamber.

The chamber is fitted with a large CHA analyser of 150mm radius. Prior to entering the analyser, the photoelectrons are focussed by a lens, included for improved collection efficiency and to allow the analyser entrance slit to be mounted further away from the sample, primarily for better sample access by the various radiation sources. The analyser is fitted with selectable entrance slits, from 6mm to 1.5mm in width. Electrons are counted by a channel electron multiplier (channeltron) at the analyser exit aperture.

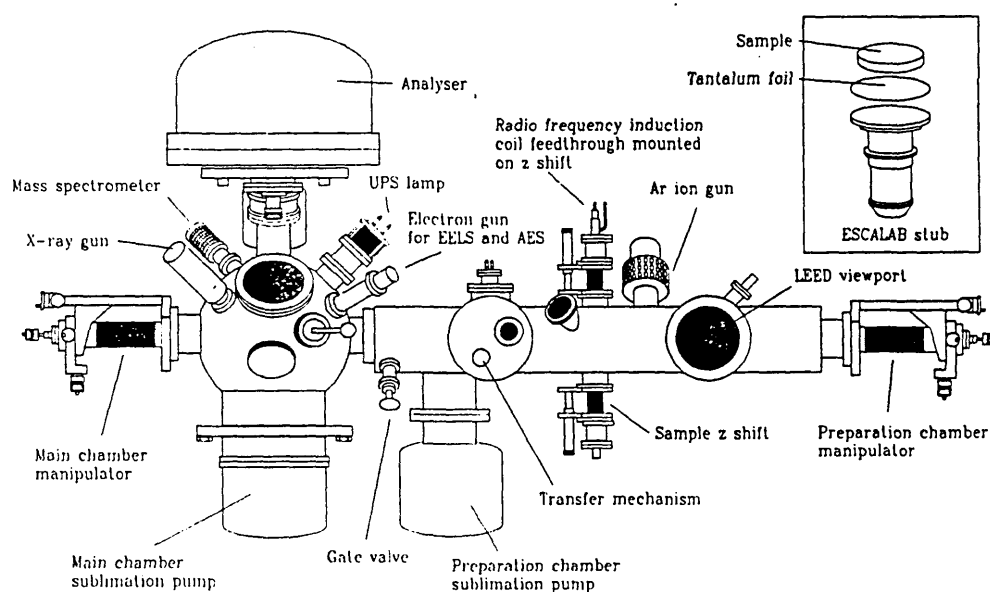


Figure 3.2: Drawing of the VG ESCALAB in the configuration used in the present work. Inset is shown a typical stub mounting arrangement which allow sample movement within the vacuum chambers. The sample is secured to the stub by spot welding with Ta wire.

The preparation chamber contains the sample preparation facilities. Samples which clean spontaneously upon heating may be moved into a Leybold-Heraeus coaxial water cooled radio-frequency (r.f.) induction coil mounted in this chamber. Power is supplied by a 1.5kW 470kHz generator. It is possible to attain specimen temperatures in excess of 1500°C in this way. The induction method also confers the advantage that samples can be heated in any atmosphere, from 10^{-10} -100torr of gas, including oxygen and hydrogen.

The chamber is equipped with a long travel manipulator and a three grid LEED optics. A Penning type ion gun is used to bombard the sample (sputter) with noble gas ions of between ≈ 2 and 10keV energy, usually Ar^+ . In the Penning discharge, the confinement of argon atoms in a strong magnetic field produces a stream of positive ions at the cathode. These are extracted and focussed onto the sample electrostatically. Very large sputter ion energies disrupt the surface order to a large extent and a brief anneal in the r.f. coil is usually performed subsequently. Mechanisms of surface sputtering are discussed later.

A gate valve separates the preparation chamber from the fast-entry lock at the rear of the machine. The fast-entry lock is equipped with a similar transfer system as the preparation chamber and can be opened to atmosphere without significantly affecting the preparation chamber pressure. A bakeable gas manifold is fitted behind the fast entry lock which can either be UHV pumped. It has a variety of inlet sites and gas can be admitted to either of the chambers through precision leak valves from here.

3.6.3 Calibration

The ESCALAB was calibrated by measuring the binding energy of the $\text{Ag:3d}_{5/2}$ peak of a clean Ag polycrystalline surface at $368.30 \pm 0.05 \text{ eV}$ by $\text{Mg K}\alpha$ XPS as shown in figure 3.3. This is within 0.1eV of the quoted binding energies in Briggs and Seah^{3,8}. The spectrum of the Ag:3d region is accompanied by satellite structure associated with the anode. The experimental resolution was estimated to be 0.9-1eV under typical measuring conditions of pass energy and slit size from the broadening of the Fermi edge from a clean Co surface.

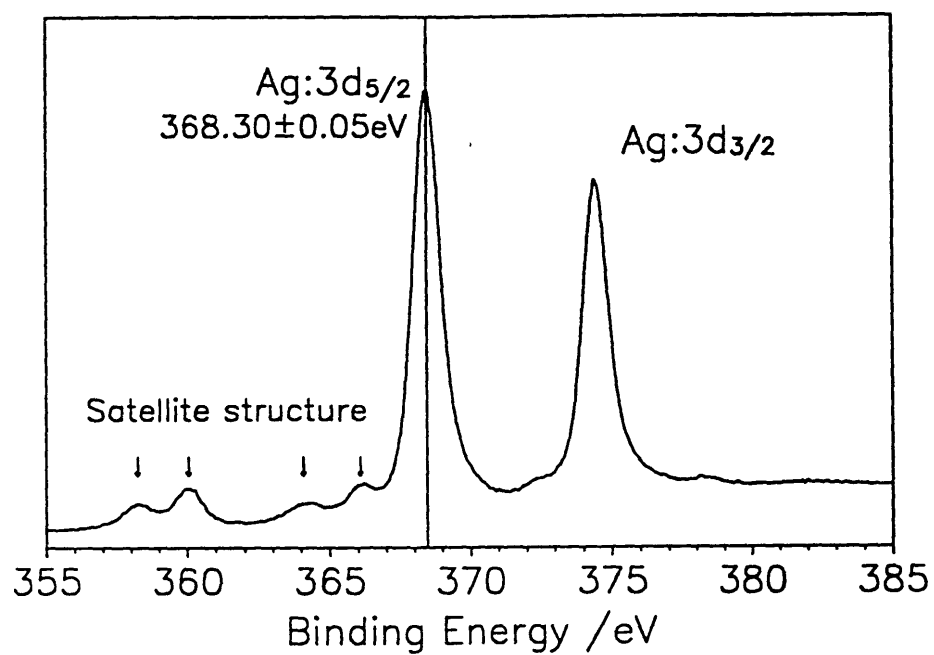


Figure 3.3: Mg XPS spectrum of 3d region of Ag used to calibrate the ESCALAB spectrometer, showing the presence of anode x-ray satellite structure.

3.6.4 Sensitivity Factors for Quantitative XPS

The empirical photoelectron sensitivity factors of the Ti:2p, Co:2p and O:1s peaks were determined experimentally by Mg K α XPS measurements on clean Ti, clean Co and on a perfect TiO₂(110) surface. The sensitivity factor is proportional to the photoelectron ionisation cross section σ as discussed in chapter 2, after correcting for electron pathlength and sample density, but also depends on the analyser transmission function. The relative experimental values determined here agree quite closely with published values of ionisation cross sections as indicated by table 3.1. Comparison with such sub shell ionisation cross sections indicates that sensitivity factors are largely dependent on cross sections.

A value for the C:1s sensitivity factor was not experimentally determined here, and so a value of 6.68 was used as an average of the experimentally determined measurements given above.

3.7 The Leybold-Heraeus HREELS System

In contrast to the multi-technique VG ESCALAB, the Leybold UHV system is a single chamber design with four levels of surface analysis features. The front and rear views of the spectrometer are given in figure 3.4 and 3.5. There is a main vertical chamber containing the HREELS system itself and a horizontal section containing the other surface analytical instrumentation. The chamber is pumped by a turbomolecular pump and an ion pump mounted directly below the HREELS assembly. The space above the ion pump houses the titanium sublimation pump and is enclosed by a liquid nitrogen coolable jacket. Routine pressure is 8×10^{-11} mbar. The lowest pressure experienced was 2×10^{-11} mbar, which probably represents the gauge x-ray limit (lower than the ESCALAB conventional ion gauges owing to the 'extractor' design).

The chamber does not have facilities for fast entry and exit of samples as does the ESCALAB, and so with every change of sample, the system is vented using dry N_{2(g)}. Samples are mounted directly on the end of a long-travel manipulator in a way unique to each sample. The sample mount is tailored to the treatment that the sample will experience once under

Table 3.1: Sensitivity Factors for Mg K α XPS (relative to Ti:2p=1.00)

Co:2p	O:1s	C:1s	Ref
0.47	2.72	7.1	3.9
1.0	2.0	4.8	3.10
-	2.71	6.71	3.11
0.50	2.74	7.6	3.11
-	2.71	6.88	3.12
0.43	2.77	7.9	3.13
0.47	2.36	-	This work

Notes on References

- 3.9 Empirically derived atomic sensitivity factors from experimental data.
- 3.10 Relative photoelectron signal heights (major line) obtained directly from Al K α and Mg K α excited XPS spectra. No other considerations.
- 3.11 Relative sub shell photoionisation cross sections as determined experimentally (first set) and as calculated (second set).
- 3.12 Relative peak heights measured with a Varian spectrometer. No other corrections.
- 3.13 Calculated sub shell photoionisation cross sections for Mg K α and Al K α XPS

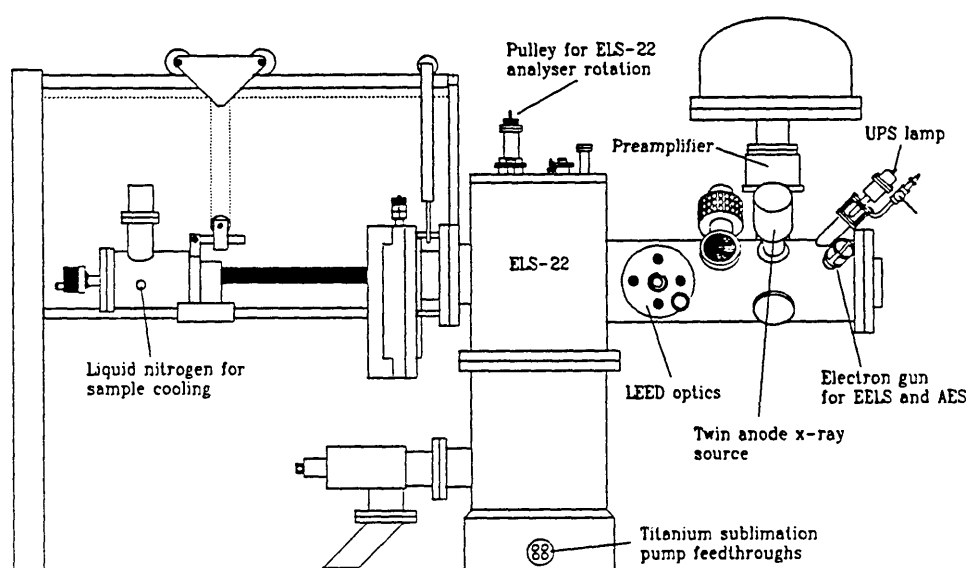


Figure 3.4: View of the Leybold-Heraeus vacuum system which houses the ELS-22 HREELS optics.

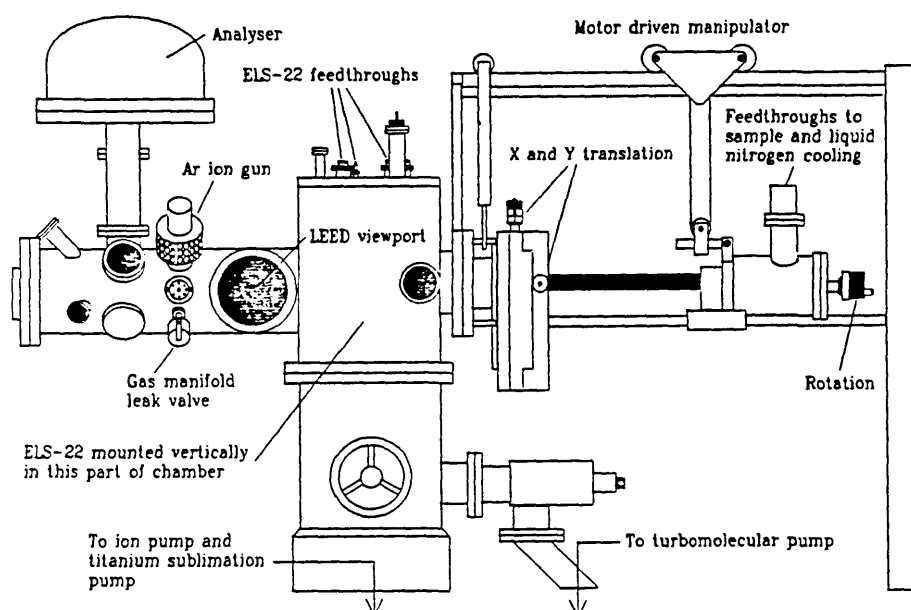


Figure 3.5: Rear view of the Leybold-Heraeus vacuum system.

UHV. Sample cleaning and subsequent gas exposure is performed in the one chamber. Sample mounting (as discussed later) is crucial to the successful operation of each experimental session.

3.7.1 Surface Analysis Facilities

At one position in the UHV chamber, analysis is based about a Leybold-Heraeus EA 10 concentric hemispherical analyser. The 100mm radius analyser has a 2mm fixed entrance slit. Electron counting is by a 'venetian blind' type electron multiplier fixed at the exit aperture. There is a cylindrical pre-analyser lens. Collection efficiency is poorer than the VG ESCALAB and hence, all high resolution XPS was performed in the VG machine. XPS is excited by a conventional VSW twin anode (Mg/Al) x-ray source operated at 200W. Also mounted here are a Leybold-Heraeus 500eV to 5keV electron gun for AES or low resolution energy loss spectroscopy (electronic EELS), a gas discharge lamp and a VG Masstorr 300 atomic mass unit quadrupole used for residual gas analysis.

At a second position in the chamber is a VG AG21 Penning discharge ion gun, identical to the one in the ESCALAB. Here the sample can be sputtered by Ar ions at 2-10keV incident energy. As a precaution, thermal treatment of the sample was performed at this level, since evaporation here is unlikely to lead to vapour deposits on any of the main surface instruments.

A third part of the system contains conventional three grid LEED optics and a large observation viewport. A shutter covers the optics during any thermal treatment. The large window allows the sample to be viewed whilst heating occurs and, if necessary, allows direct line of sight by an infra-red pyrometer for sample temperature measurement.

3.7.2 The ELS-22 Construction

By retracting the horizontal manipulator to its furthest extent, the fourth level of instruments can be accessed. It is here that the vertically mounted Leybold-Heraeus ELS-22 HREELS optics are situated. A schematic of the assembly is shown in figure 3.6. It is of a double tandem

127° cylindrical sector design with variable sample and analyser geometry. The assembly is fabricated of copper and all inner surfaces are coated with gold to prevent the build-up of unwanted stray charge. The analyser unit is suspended on a pulley which allows it to be rotated relative to the monochromator through 60° for setting-up and off-specular work. All conducting leads are insulated by glass-fibre shrouds. The whole assembly is magnetically and electrically isolated by a double μ -metal shield^{3,14}.

Near the top of the chamber is a high precision electron gun. The filament is fashioned into a 'V' shape and electrons are extracted from the tip by a dish shaped repeller which sits around the filament allowing only the tip to protrude. The repeller is at a slight negative potential with respect to the filament. The electrons are then accelerated through three anodes (a_1 , a_2 , a_3), each of which has a continuously variable asymmetry control (changing the potential on one side of the anode relative to the other) and the monochromator entrance slit M. The monochromation of the electrons is performed by two 127° cylindrical sector analysers (pre-monochromator pm and main-monochromator mm) of radius 50mm arranged consecutively, and electrons with the pass energy are transmitted. The pass energy of each of the monochromators can be set independently, but is typically 150-250meV. Finally, the electrons are accelerated to the primary beam energy of between 1 and 50eV by two accelerating anodes (e_1 , e_2) before impacting the earthed (E_0) sample.

The reflected electron beam enters the analyser optics by first passing through two deceleration electrodes (e_3 , e_4) and analyser slits (A). As in the monochromator, two 127° spherical sector analysers mounted in tandem perform the electron energy selection. Again, electrons with a pass energy of typically 200-300meV are passed. The pass energy of these (main-analyser ma and second-analyser sa) can be set independently of each other, but by using a ramp control, can be swept in tandem over an energy range, typically from 0 to -500meV from the primary beam energy. Electrons are counted by a channeltron multiplier at the final exit aperture A of the second sector.

In this research, the primary beam energy was usually set to 1 or 2 eV. Some work was carried out at 5eV and higher beam energy. Lowering the beam energy always improved the count rate. The sample geometry

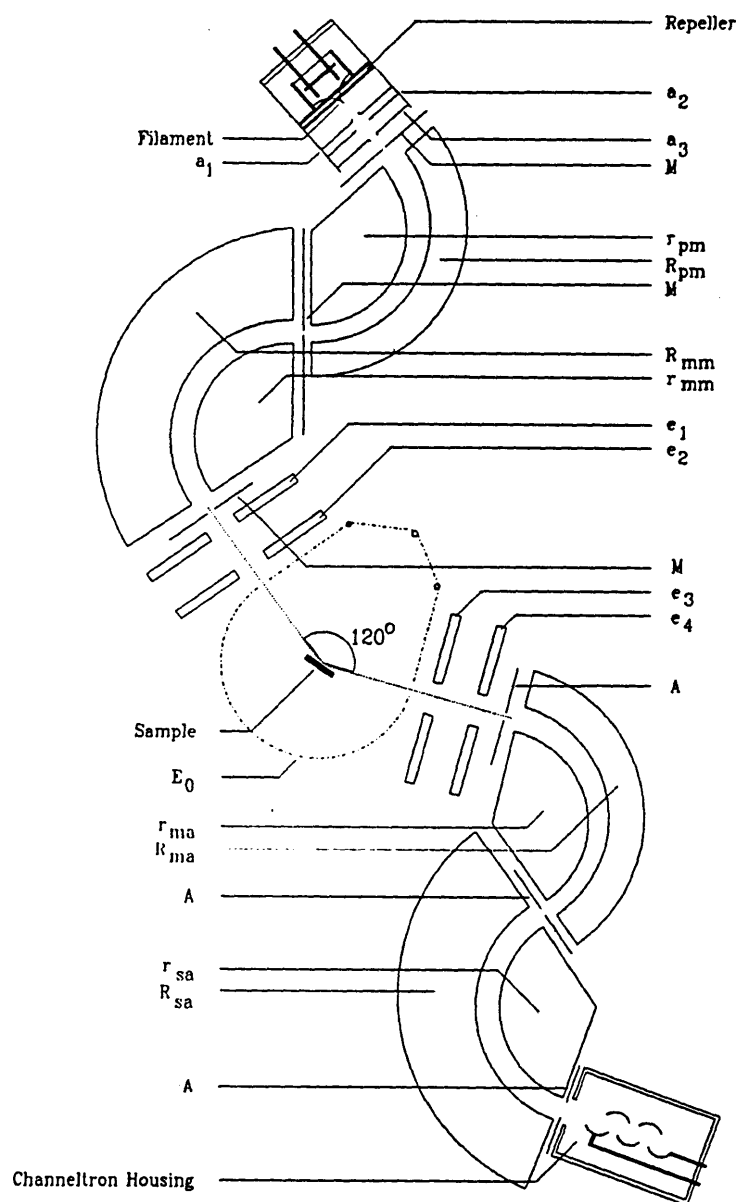


Figure 3.6: Drawing of the ELS-22 HREELS spectrometer. In the chamber, the electron gun is mounted uppermost. The analyser assembly can be rotated by means of a pulley system but was operated in the 'specular mode' shown here with the angle between the incident and scattered beams at $\approx 120^\circ$. See text for explanation of symbols.

throughout this work was fixed at an incident and reflected beam angle equal to 60° from the sample surface normal. The current at the sample is typically $1\text{--}3 \times 10^{-10}\text{A}$. The exit slit from the monochromator and the entrance slit of the analyser is $1 \times 4\text{mm}$ setting a minimum sample diameter of approximately 4mm .

In the 'straight through' geometry used to set up the optics initially, the monochromator exit and the analyser entrance are set 'in line' so that electrons travel directly into the analyser without impinging a sample. Count rates were often in excess of $2 \times 10^5\text{s}^{-1}$, the saturation level of the channeltron. Under these circumstances, count rates from a well annealed flat sample at the elastic peak were typically $4\text{--}12 \times 10^3\text{s}^{-1}$ with 7meV FWHM. A level of more than $20 \times 10^3\text{s}^{-1}$ was considered exceptional and below $3 \times 10^3\text{s}^{-1}$ unworkable.

3.7.3 Calibration

The binding energy scale of the Leybold spectrometer was not calibrated in this study. However, measurement of some Ag photoelectron peaks has been performed by a previous worker and the $3d_{5/2}$ binding energy was measured at $368\text{eV}^{3,15}$. Measurements of the $\text{Ti:}2p_{3/2}$ binding energy on a clean $\text{Ti}(0001)$ surface gave a binding energy of $453.9 \pm 0.2\text{eV}$, in good agreement with the ESCALAB data measured at $453.85 \pm 0.05\text{eV}$. The ramp output of the HREELS ELS-22 control module was checked by digital voltmeter. The indicated and measured millivoltage was found to be within 2%.

3.8 The Inverse Photoemission (IPES) System.

This vacuum system comprises a single 300mm diameter chamber with VSW 50mm radius CHA analyser with fixed 2mm slits and an electron transfer lens. The sample mounting is similar to that of the HREELS chamber, but the manipulator is arranged vertically in this instance. Heating is effected resistively by passing current across the sample. The system incorporates a VSW EG5 electron gun which operates at $\approx 200\text{eV}$ to 5keV energy which was used for AES measurement in combination with the CHA. Also fitted is a VSW filament-type ion bombardment gun which operates at fixed 500eV energy and $\approx 5 \times 10^{-6}\text{mbar}$ Ar pressure. Sample current was

typically 2-5 μ A under these conditions. Gas is supplied from high purity Messer-Griesheim pressure cans and admitted to the chamber via a precision leak valve mounted close to the ion gun. The chamber is pumped by diffusion pump, liquid nitrogen cooled titanium sublimation pump and appendage ion pump. Base pressure is typically 2×10^{-10} mbar.

3.8.1 Sensitivity Factors for Quantitative AES

Sensitivity factors used to determine elemental concentrations by AES measurements were taken from the elemental sensitivity factors[◇] deduced by Payling^{3.16} quoted as,

$$\text{C KVV (272eV)} = 0.10$$

$$\text{Ti LMV (417eV)} = 0.35$$

$$\text{O KVV (515eV)} = 0.31$$

$$\text{Co LVV (773eV)} = 0.19$$

Therefore the sensitivity of Ti with respect to C is 3.5, with respect to O is 1.13 and with respect to Co is 1.84. Correcting these figures for differences in electron escape depth using the relationship for the electron mean free path $\lambda = KE^{0.75}$, as the average value of both the empirical models and the experimentally determined variation of sampling depth with kinetic energy $KE^{3.17}$ gives the sensitivity factors,

$$\text{Ti/C} = (0.35/0.10) \times 1.38 = 4.83$$

$$\text{Ti/O} = (0.35/0.31) \times 0.85 = 0.96$$

$$\text{Ti/Co} = (0.35/0.19) \times 0.62 = 1.15$$

The Payling sensitivity factors used in the calculation were derived from Auger spectra recorded with a beam energy of 5keV, much greater than the 2keV used in the present work. The variation of the peak-to-peak height $N'(E)$ with beam energy^{3.18} shows that the Ti, Co and O peak sensitivities are all reasonably constant over the range 2 to 5keV beam energy. So the calculated factors can be directly applied to the experimental data. However, the $N'(E)$ height of the C:KLL Auger measured with a primary electron beam energy of 5keV is very much reduced if measured at 2keV. An

[◇] Modified for differences in elemental densities only

See Erratta→

experimentally determined sensitivity factor^{3.19} has been determined using TiC with a 3keV incident electron beam energy. This value, corrected for sampling depth gives $Ti/C = 1.6$.

3.9 Sample Mounting and Pretreatment

3.9.1 The Samples.

The single crystal CoTi was supplied by Goodfellow Metals (Cambridge) in the form of two 1mm thick discs of 5mm diameter. The specimens were cut from a rod grown by pulling from a molten mixture ($5mm\ hour^{-1}$)^{3.20} of the two pure metals under an Ar atmosphere (Czochralsky technique). The crystallographic orientation was determined by a Laue back-reflection technique which indicated that the desired 110 face was within 4° of the surface plane. One slice was prepared for mounting in the ESCALAB and the other for the HREELS system.

The Ti single crystal was obtained from Metal Crystals Ltd. (Cambridge) and was 4mm in diameter and 0.5mm thick. The 4mm diameter is comparable with the HREELS analyser entrance aperture and, as such, is probably the minimum sample dimension that can be used. It was grown in a similar manner to the CoTi sample and was prepared for HREELS mounting as discussed below.

The titanium (>99.6%) and cobalt foil (>99.99%) used, obtained from Goodfellow Metals, was used without further treatment. Single crystal $TiO_2(110)$ (rutile), with about $10mm^2$ surface area, was obtained from Hrand Djehahindjian (Monthey, Switzerland). It had been previously polished^{3.10} to a high optical finish. The sample was oxidised by heating in air at $\approx 1000^\circ C$ for 24 hours to ensure stoichiometry prior to *in vacuo* treatment at which time it became colourless.

The two Co-Ti alloys, $CoTi_2$ and Co_3Ti , were prepared by melting the appropriate masses of the constituents in an arc furnace. About 10g (total) of the two metals were melted under an argon atmosphere ($\approx 100mm$ Hg) in a water cooled copper hearth. The removal of any residual oxygen in the argon atmosphere was achieved by melting a small 'getter' button of Ti

metal a few times. The sample buttons were remelted and turned three times to ensure homogeneity. Sample oxygen content was crudely gauged by comparing pre and post-melt total masses. The oxide component of the Co_3Ti sample was estimated at 0.071% (710 ppm) whilst that of the CoTi_2 at 0.052% (520 ppm). The buttons were cut on a slitting machine using a silicon carbide cutting disc using a water based coolant/lubricant to form one specimen from each button approximately 1mm thick and 7-9mm in diameter.

In addition, the samples were analysed by x-ray diffraction in a Siemens Diffraktometer to examine phase purity using $\text{Cu K}\alpha_{1,2}$ radiation. The x-ray diffraction patterns obtained from the polished samples are given in figure 3.7. The diffraction patterns obtained directly after fabrication and after a period of annealing in the ESCALAB preparation chamber in a vacuum of 10^{-8} mbar or better were compared with standard x-ray powder diffraction files for Co-Ti, Co-Ti-O, Co-Ti-C (none), Co-O and Ti-O compounds. The patterns obtained indicated the presence of multiple phases, but in both annealed samples, all the most intense peaks corresponded to the desired phases as shown in tables 3.2 and 3.3. Phase purity was improved upon annealing. A minor Co_2Ti phase and some Co were detected in the Co_3Ti pattern whilst the Ti_2Co sample contained some Ti together with small concentrations of other phases. No bulk Co or Ti oxides were detected.

The final stage of alloy sample preparation before entry into the vacuum systems was polishing using diamond paste down to $0.25\mu\text{m}$ grit size on a conventional lapping and polishing machine using a water based lubricant. The sample were dismounted and remounted between each grit size change to minimise cross-contamination. A final wash in propan-2-ol in an ultrasound bath followed by rinsing with de-ionised water completed the pretreatment. The Ti and Co foils were left unpolished but were washed in water and propan-2-ol before entry to the UHV chamber. Photographs of the Co-Ti alloys are shown in figure 3.8.

3.9.2 Mounting

In the case of samples destined for the ESCALAB spectrometer, the specimens were secured to a suitable stub (Ni or Mo) using $0.25\text{mm } \phi$ Ta

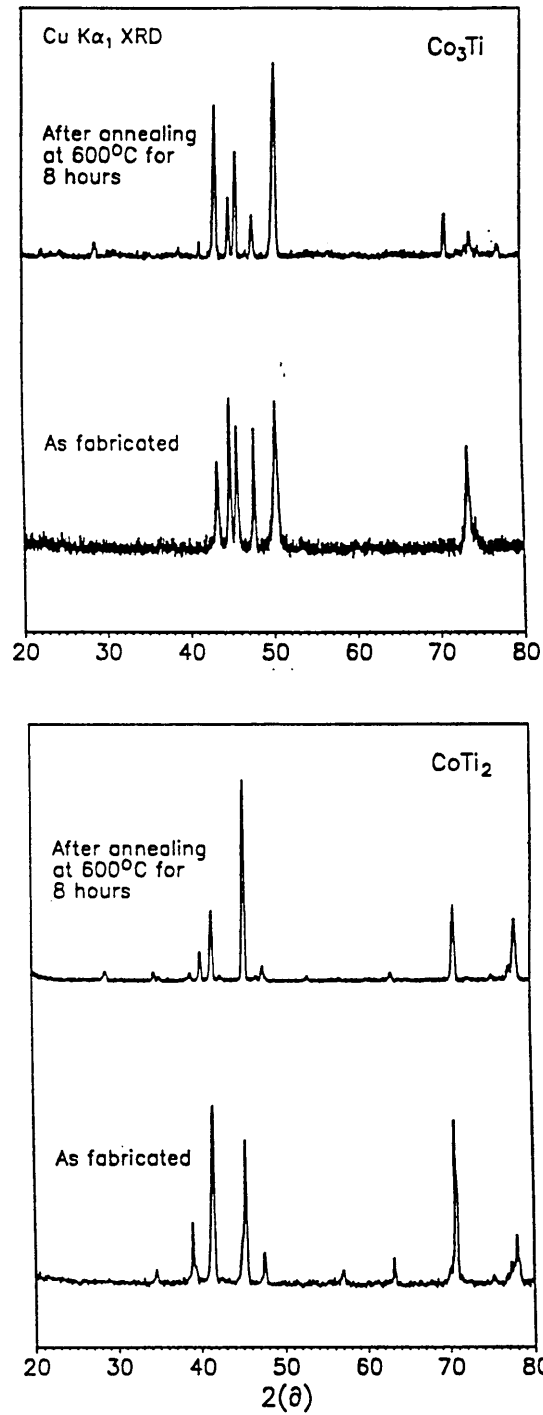


Figure 3.7: X-ray diffraction patterns of Co_3Ti and CoTi_2 as fabricated, and after annealing at $<10^{-9}$ mbar and 600°C for 8 hours.

Table 3.2: X-ray diffraction patterns obtained from annealed alloy samples

Sample	Intensity	$2(\theta)$	d (Å)	Expected?
CoTi ₂	100	45.48	1.99	√
	38	70.78	1.33	√
	36	41.64	2.17	√
	31	78.07	1.22	√
	16	40.27	2.24	
Co ₃ Ti	100	50.39	1.81	√
	79	43.28	2.09	√
	55	45.78	1.98	√
	30	44.95	2.01	
	23	71.01	1.33	
	22	47.73	1.90	
	12	74.01	1.28	√

√ Expected from comparison with standard XRD patterns of these compounds. Joint Committee on Powder Diffraction, International Centre for Diffraction Data, Swarthmore, PA, USA, 1989

Table 3.3: Characteristic d spacings of Co-Ti-O compounds from standard XRD patterns

Compound	d spacing (Å)		JCPD Ref*
	Primary Intensity	Secondary Intensity	
Co ₃ Ti	2.08	1.09	23-0938
Co ₂ Ti	2.02	1.18	28-0381
CoTi	2.25	1.32	5-0719
	2.10	1.22	12-0083
CoTi ₂	2.17	1.33	7-0141
Co	1.91	1.25	5-0727
	2.05	1.77	15-0806
CoO	2.13	2.46	9-0402
Co ₃ O ₄	2.44	1.43	9-0418
CoOOH	4.38	2.31	7-0169
Co(OH) ₂	2.37	1.77	30-0443
Ti	2.24	2.56	5-0682
TiO	2.07	1.46	9-0240
Ti ₂ O ₃	1.70	2.57	9-0309
Ti ₄ O ₇	3.21	2.82	18-1402
TiO ₂ Anatase	3.52	1.89	21-1272
Rutile	3.24	1.69	21-1276
Brookite	3.51	2.9	29-1360
Co ₂ Ti ₄ O	2.16	1.33	5-0697
CoTiO ₃	2.73	2.53	15-0866
Co ₂ TiO ₄	2.55	2.99	18-0428
CoTi ₂ O ₅	3.48	2.76	35-0793

*JCPD Ref = Card Number, Joint Committee on Powder Diffraction, International Centre for Diffraction Data, Swarthmore, PA, USA, 1989

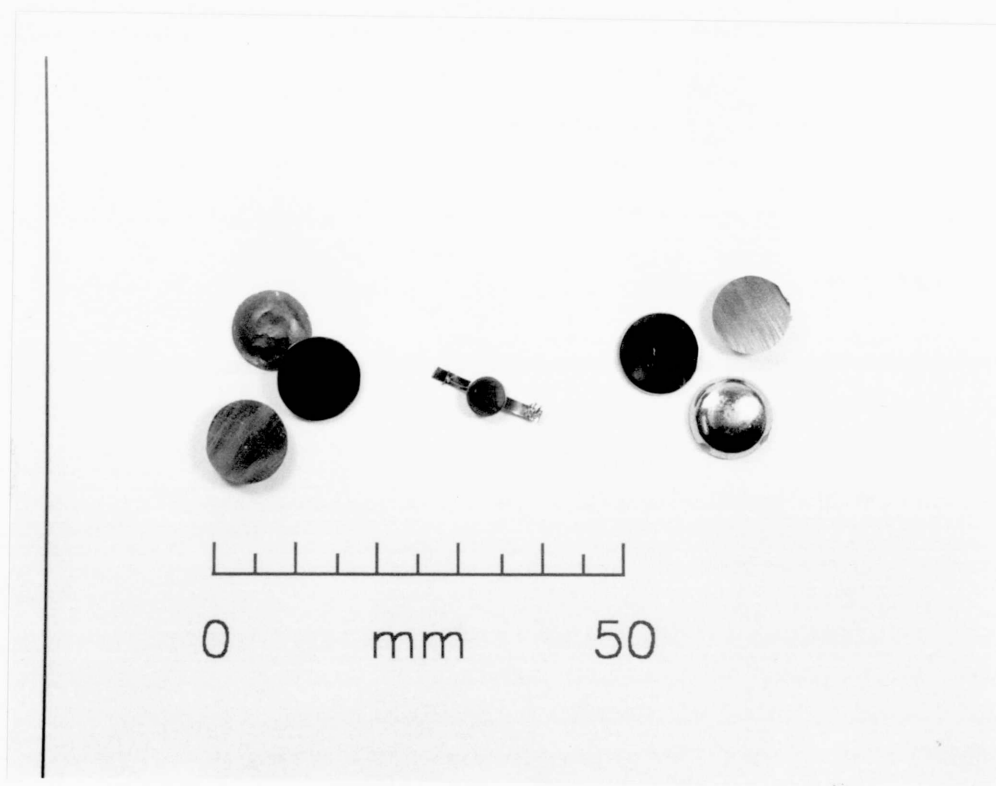


Figure 3.8: Photographs of the alloy buttons (CoTi_2 left, Co_3Ti right) and samples after slitting (darkest discs). The single crystal $\text{Ti}(0001)$ with the laser welded Ti backing foil is shown in the centre.

wire (>99%) in such a way as to minimise sample face obscuration. The wire was attached to the stub by spot-welding under argon or helium.

In order to provide some access for physical mounting of the HREELS samples without jeopardising them by welding connections directly, small backing ribbons (Ta in the case of the CoTi sample and Ti in the case of the Ti sample) were CO₂ laser welded to the sample rear. The laser welding was performed by Thorn EMI (Hayes, Middlesex) and involved the pinning of the backing to the sample rear by melting the edges of the former at precisely defined spots. Caution was taken to use a low laser power to reduce the possibility of sample melting. Unfortunately, the 0.5mm thick Ti(0001) crystal did become holed through to the surface in one place by the laser. This did not appear to affect the HREELS performance in later experimentation.

The sample mount used for the HREELS experiments (or for use in the IPES system) was of a more complex design as displayed in figure 3.9 and in photographs in figure 3.10. The sample was strung between two 2mm ϕ Ta rods, each $\approx$ 150mm long, using Ta wire. These were fixed to a ceramic block which was connected to the manipulator, electrically isolating the rods. Current could be passed through the sample by making electrical connections to each rod via the manipulator. For sample cooling, a 5mm ϕ copper rod was bolted to the manipulator. The other end was attached to the sample backing using Cu braid or thin Cu sheet. Electrical isolation was maintained by a single crystal sapphire held in a break in the copper rod. This made possible good thermal conductivity and good electrical insulation. The HREELS manipulator carries six isolated electrical feedthroughs and allows liquid nitrogen to circulate inside for cooling. Some evaporation of the thin copper sheet or braid onto the Ta rods did occur as a result of sample heating but fortunately not onto the sample surface itself. Sample temperature was judged by a chromel/alumel thermocouple welded to the backing ribbon as close as possible to the specimen. An infra-red pyrometer was also used on occasion with a previously calibrated emissivity ϵ of 0.18 for CoTi.

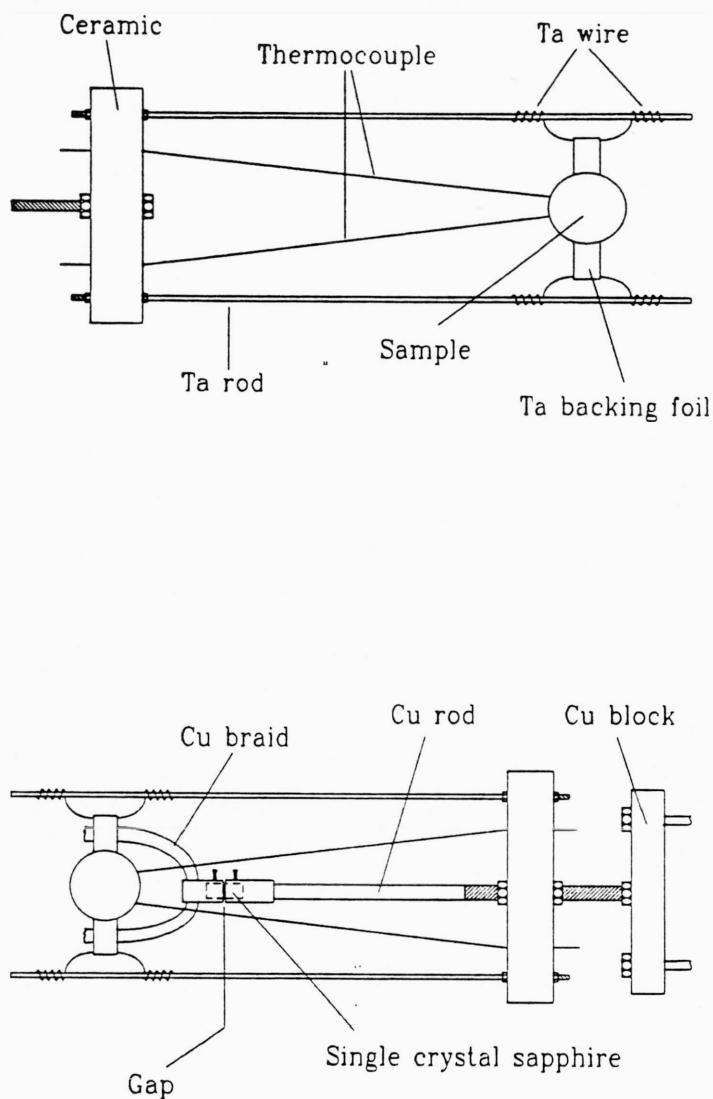


Figure 3.9: Drawing of the sample mounting for the HREELS spectrometer. The top view shows the normal assembly complete with thermocouple whilst the lower view shows the additional Cu rod necessary for efficient thermal contact with the sample. The rod is fitted with a single crystal sapphire to maintain electrical isolation.

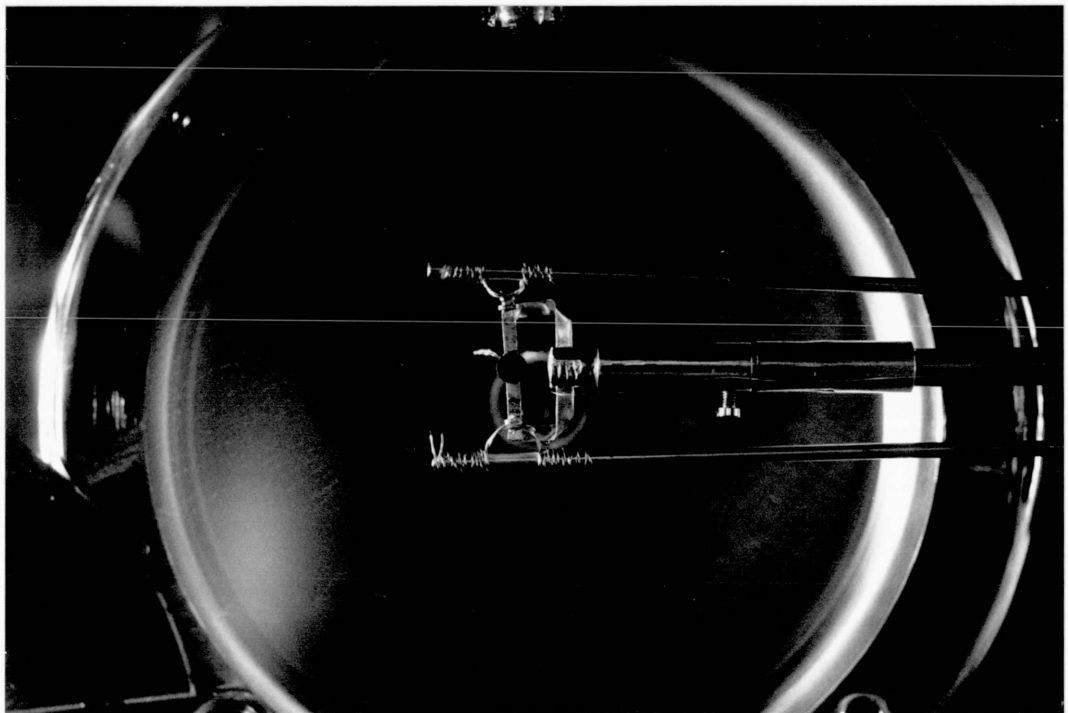
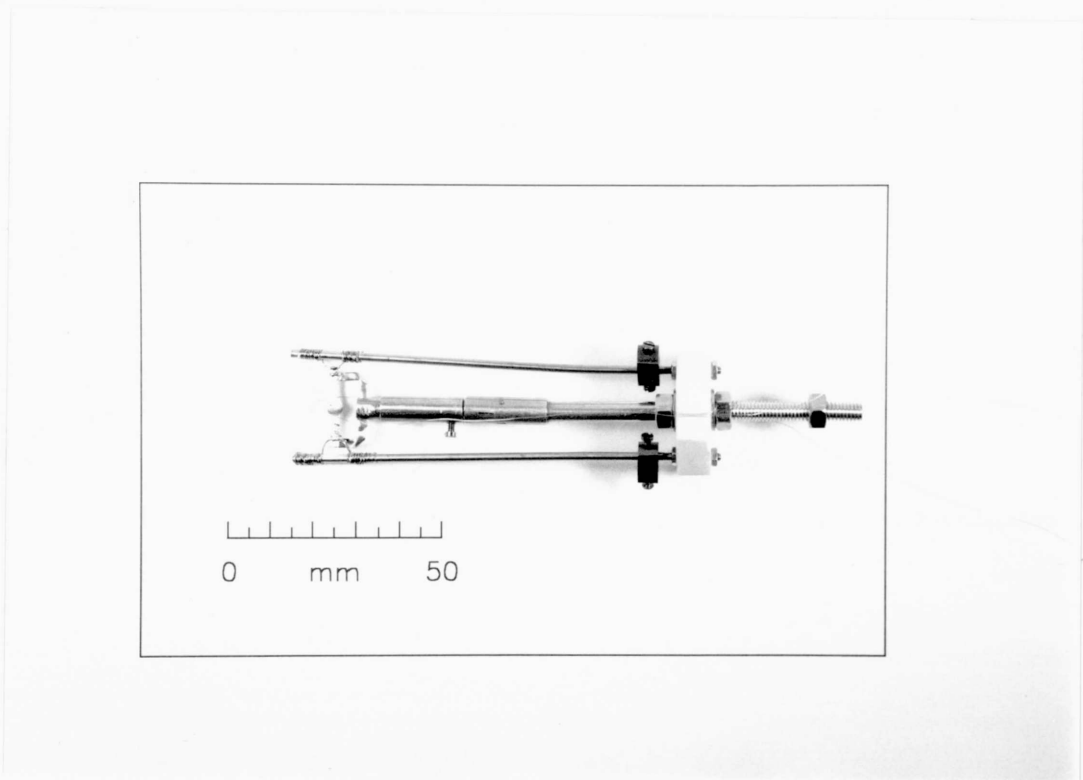


Figure 3.10: Photograph of the sample mounting arrangement (top) and in place in the Leybold-Heraeus vacuum system (bottom).

3.10 References

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4. The Oxidation of Ti Metal

4.1 Surface Preparation

All experimentation involving high resolution XPS measurement (sections 4.2-4.5) was performed on the polycrystalline Ti foil or single crystal $\text{TiO}_2(110)$ in the VG machine. All HREELS (section 4.8-4.9), together with the necessary XPS work for surface characterisation prior to analysis by other techniques, was performed on the $\text{Ti}(0001)$ single crystal in the Leybold-Heraeus system. The XPS spectra of both Ti foil and single crystal substrates were essentially identical.

The surface of Ti foil as obtained directly from the supplier, was examined by $\text{Mg K}\alpha$ XPS in the VG ESCALAB. Core peaks due only to C and O contamination were observed. The mechanically polished $\text{Ti}(0001)$ single crystal, examined in the HREELS system, also showed intense C and O signals but did show some complex Ti:2p structure. Removal of contaminants was first attempted by cycles of Ar^+ bombardment (2keV, 20 minutes) followed by brief annealing at $\approx 600^\circ\text{C}$ (5-10 minutes). Both the single crystal and polycrystalline surfaces after such a treatment always showed weak S:2p structure (see figure 2.4 previously), although the concentration of C and O gradually decreased.

Sulphur segregation was encouraged by heating the sample to 600°C in $<10^{-9}$ mbar vacuum for 72 hours in the case of the single crystal or 24 hours in the case of the polycrystalline foil. It has been reported that C and O dissolve into the Ti bulk under these conditions, leaving negligible concentrations at the surface^{4.1}. After this prolonged anneal, core level XPS showed no measurable C or O intensity at all but structure due to Ti and S as shown in figure 4.1. All S intensity was completely eradicated by light Ar^+ sputtering (2keV, 5minutes) followed by a brief anneal at 600°C for <60 s.

Both Ti surfaces were then free of all detectable contamination as measured by XPS. Furthermore, the $\text{Ti}(0001)$ face produced a sharp 1×1 LEED pattern as indicated by figure 4.2, while the polycrystalline foil showed visible evidence of crystallisation but gave no LEED pattern. Once prepared in this way, a clean surface could be easily recovered by heating the sample

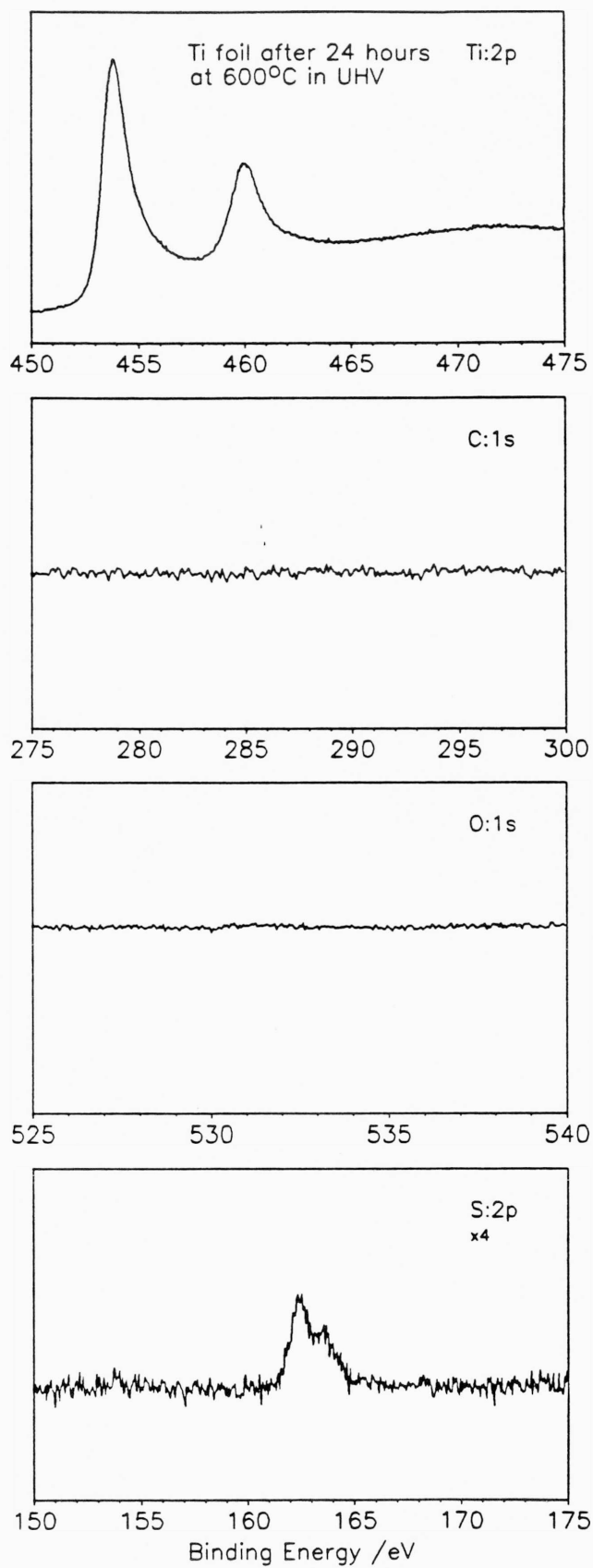


Figure 4.1: Mg core level spectra of Ti foil heated to 600°C *in vacuo* for 24 hours showing surface segregation of S.

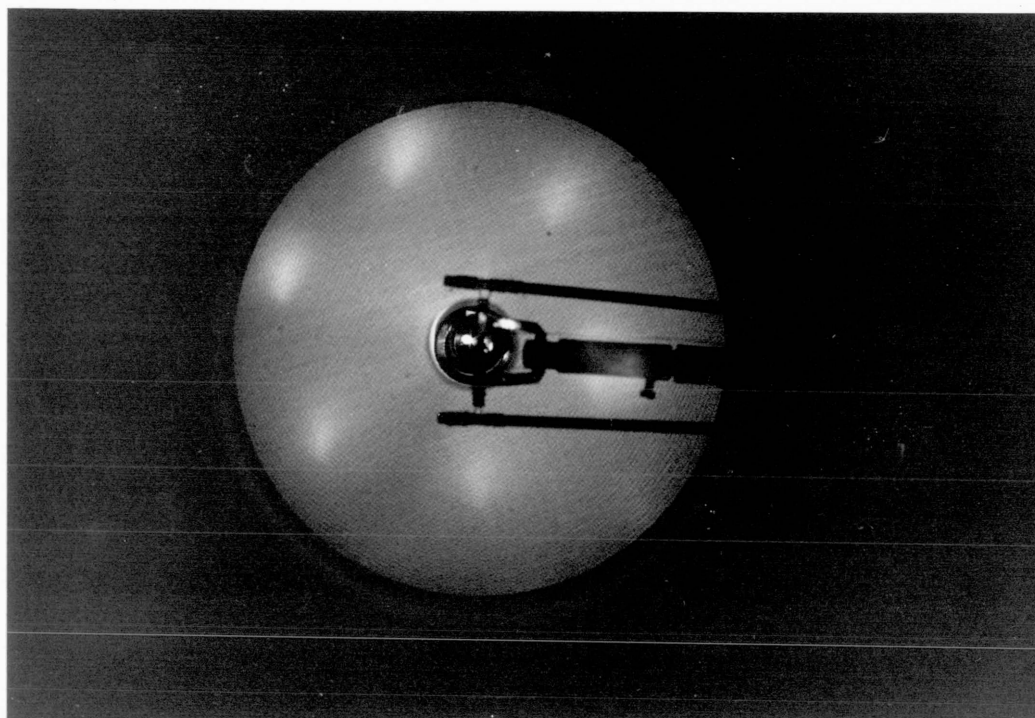


Figure 4.2: 1x1 LEED pattern of Ti(0001) surface after surface preparation.
 $E_p = 93\text{eV}$.

to $\approx 600^\circ\text{C}$ for several minutes without the reappearance of S. Figure 4.3 shows the changes to the Ti:2p and O:1s XPS spectra of clean Ti foil exposed to a moderate O_2 dose (7500L), after heating in vacuum for ≈ 5 minutes.

4.2 The Oxidation of Ti Followed by XPS.

The oxidation of polycrystalline Ti has been studied using XPS in some detail by others as discussed later, and thus an extensive series of experiments was not undertaken. However, some XPS work did prove useful in the assignment of oxide species produced by oxidation. In particular, the determination of quantities such as core level binding energies and relative sensitivity factors (which are expected to be machine dependent to some degree), allowed meaningful interpretation of later data.

The Mg $K\alpha$ excited XPS of the 2p core levels of Ti foil, free of any measurable contamination, is presented in figure 4.4(a). A suitable inelastic background has been subtracted. The $2p_{3/2}$ peak is located at 453.8eV and the $2p_{1/2}$ at $460.0 \pm 0.05\text{eV}$. Both show a marked asymmetry to the high binding energy side of the peaks which is due to low energy electron-hole pair excitations across the Fermi edge (so-called Doniach-Sunjić lineshape^{4,2}) as mentioned in chapter 2.

Also shown in figure 4.4(b) is the 2p spectrum of clean Ti foil exposed to 7500L O_2 at room temperature. Oxidation is characterised by growth of structure at 458.9eV and 464.8eV, and the appearance of O:1s intensity at 530.6eV binding energy ($\text{FWHM}^\ddagger = 1.8\text{eV}$). Growth in Ti:2p intensity is maximum at 458.9eV but smaller intensity changes are seen extending all the way down to the original $2p_{3/2}$ peak. Figure 4.4(c) shows the appropriately scaled difference data between the clean and O_2 exposed Ti surface which will be discussed further below.

4.3 The Surface of Perfect and Defected TiO_2 .

Since one possible oxidation product of Ti is titanium dioxide, the XPS spectrum of clean $\text{TiO}_2(110)$ (rutile) was also examined in the

[‡] FWHM = Full width at half maximum (intensity)

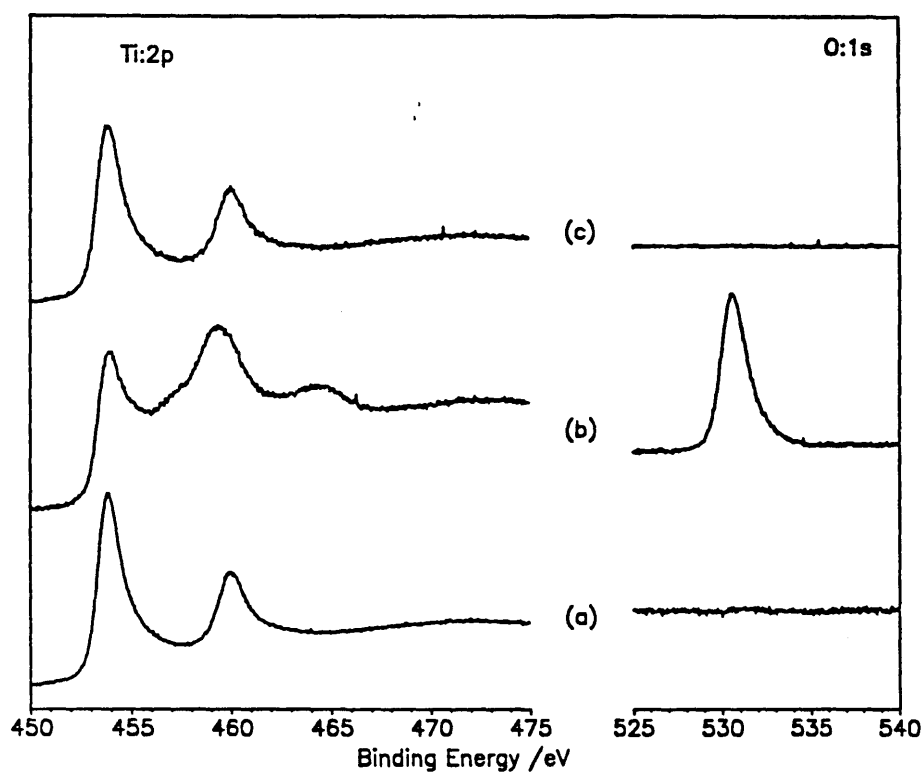


Figure 4.3: Mg XPS of Ti:2p and O:1s regions of (a) a clean Ti foil surface (b) the clean surface exposed to 7500L O₂. (c) The clean surface can be recovered after O₂ exposure by heating in the spectrometer for ≈ 5 minutes at 600°C. No S segregation is observed.

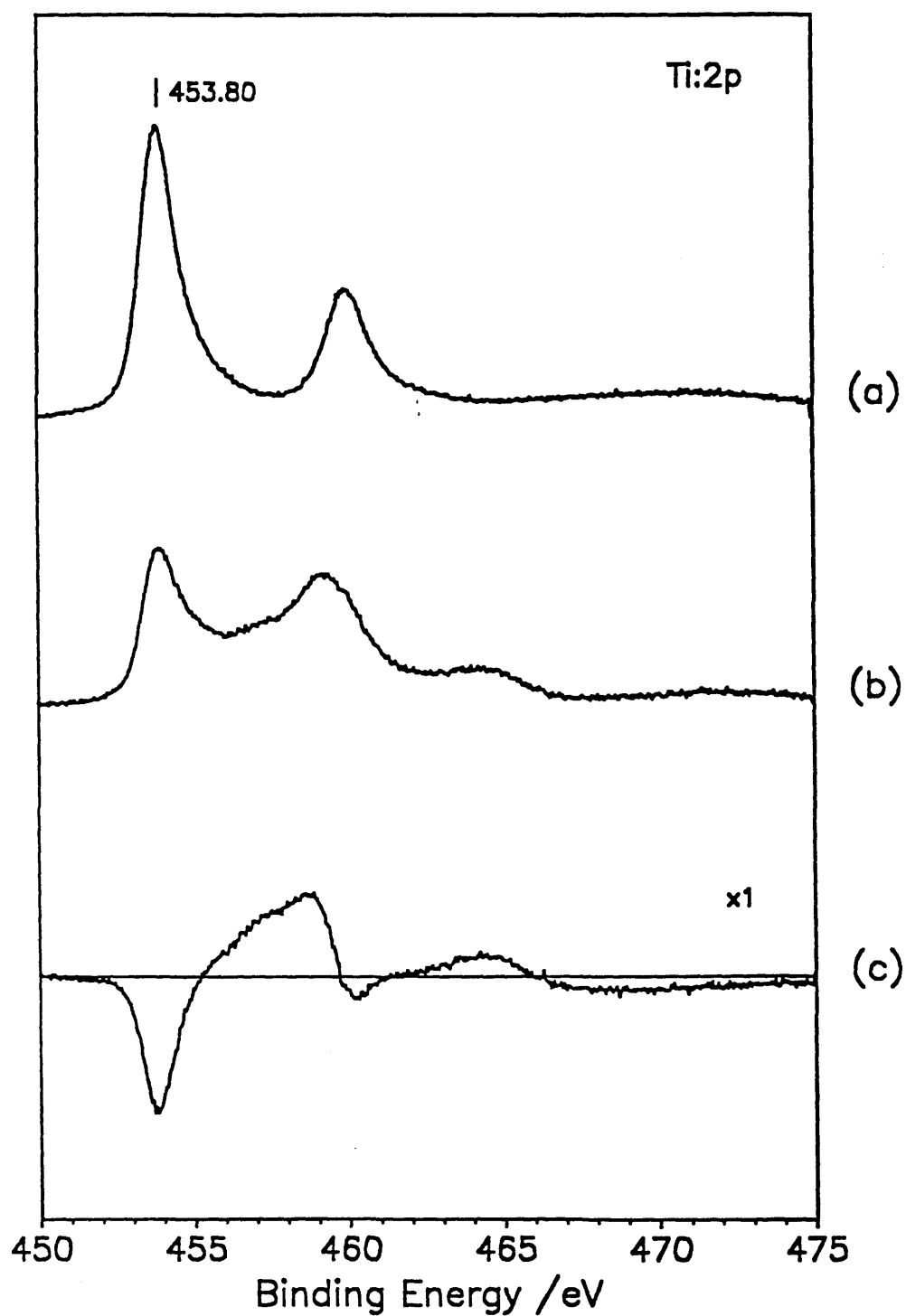


Figure 4.4: (a) Ti:2p core level spectra of a clean Ti foil surface obtained using Mg K α radiation. (b) After exposure to 7500L O₂ at room temperature and (c) difference data (O₂ exposed minus clean).

ESCALAB spectrometer.

The Ti:2p and O:1s peaks of TiO₂(110) (rutile)[§] are shown in figure 4.5. Perfect TiO₂ has no d electrons (d⁰) and a band-gap of approximately 3eV^{4,3}. Hence, the 2p asymmetry due to small-energy electron-hole excitations exhibited by Ti metal, is not seen in the lineshape of rutile and the 2p peaks are intrinsically narrower than in Ti metal (FWHM 1.4eV compared with 1.1eV in TiO₂). Unfortunately, the absence of d electrons also means that TiO₂ is an electrical insulator and thus charges to a large extent during XPS measurement. To circumvent this problem, the surface was defected slightly by bombarding with low energy Ar⁺ or He⁺ ions causing slight preferential O desorption and the creation of Ti³⁺ (d¹) defect sites. A concentration of a sufficient number of surface defect sites to prevent charging allows measurement of the true binding energy of the Ti⁴⁺ species. Comparison between the bombarded and perfect surface corrected for charging shows the presence of a 'tail' to low binding energy side of the 2p_{3/2} peak, accompanied by a general broadening in Ti:2p structure after bombardment. The concentration of Ti³⁺ species is estimated at ≈5% from O:1s and Ti:2p core level intensity changes. Consequently, it is possible to assign the Ti⁴⁺:2p doublet binding energies of 459.0 and 464.8eV for j=3/2 and 1/2 respectively. The broad low intensity feature visible at approximately 472eV is due to shake-up structure.

It is also possible to observe a subtle broadening of the O:1s peak at 530.6eV from FWHM=1.45eV in perfect TiO₂ to 1.65eV in slightly defective TiO₂. This must be due to the presence of Ti³⁺ species. These observations concur with those of defective rutile by Göpel *et al*^{4,4}. It will be recalled that oxidised Ti metal has an even broader O:1s peak (FWHM=1.8eV) than that of defected TiO₂, possibly indicative of a wider range of local Ti-O coordination environments.

4.4 Characterisation of Ti Oxides formed on Ti metal

The scaled difference between the clean and oxidised polycrystalline Ti surface is shown in figure 4.4(c). In addition to the growth of the features

[§] Two other forms of TiO₂ occur naturally - Brookite (orthorhombic) and anatase (tetragonal)

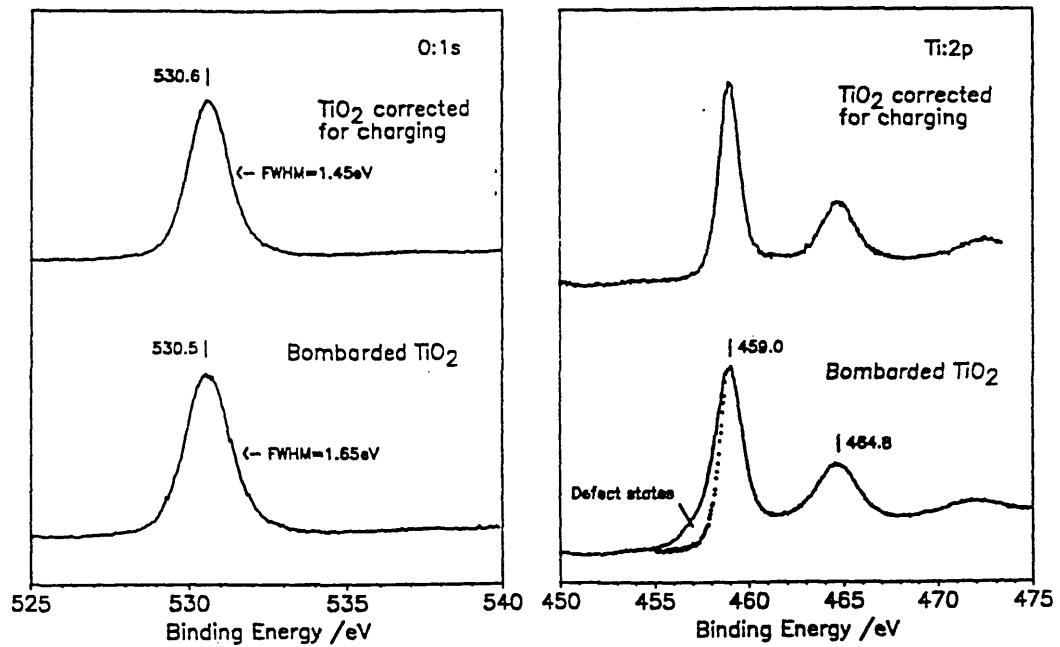


Figure 4.5: Mg XPS spectra of Ti:2p and O:1s regions of $\text{TiO}_2(110)$. The upper spectra correspond to the clean insulating surface. The lower spectra show the changes that result when the surface is lightly etched. Both spectra show a noticeable broadening upon deflection due to the presence of Ti^{3+} defects at the surface.

at ≈ 460 and 464eV as clearly seen in the raw data, the difference spectrum shows increased intensity between ≈ 455 and 460eV not obvious from a consideration of the raw spectra (a) and (b). Intensity loss is shown at the binding energy corresponding to Ti^0 (elemental Ti). Growth of intensity exists over a wide range of binding energies and is indicative of the presence of multiple oxidation states, but intensity growth is maximum at 458.9eV , very close to the experimentally measured binding energy of TiO_2 above.

The O:1s position of oxidised Ti (7500L) is similarly very close to that expected for rutile. The initial O:1s peak grows up at 531.2eV which progressively narrows and shifts down to 530.6eV after 7500L O_2 . However, the position of the O:1s peak alone cannot be correlated with the formation of titanium suboxides since the observed chemical shifts are of the order of 0.5eV and so are difficult to use as an indicator of surface oxidation products.

Even the cursory study undertaken here has demonstrated that, based on evidence of XPS binding energy, the ultimate oxidation product of Ti is TiO_2 . However, there is evidence for appreciable concentrations of suboxide species. The growth of broad structure between ≈ 455.5 - 459.5eV is indicative of the formation of multiple suboxides (monoxide Ti^{2+} , sesquioxide Ti^{3+} and dioxide Ti^{4+}).

4.5 Valence Band Features

The Mg $\text{K}\alpha$ XPS valence band regions of Ti, TiO_2 and Ti exposed to 7500L O_2 were measured and are presented in figure 4.6. The Ti:3p peak of TiO_2 is visible as a single peak (an unresolved doublet) located at a binding energy of 37.3eV . The accompanying $\text{K}\alpha_{3,4}$ satellite is visible ≈ 9 - 11eV to lower binding energy. The O:2s and 2p peaks can be seen at 22.5eV and ≈ 4 - 8eV respectively. There is no measurable density of states (DOS) at E_F as one would expect from this material. As has already been mentioned, the practicalities involved in measuring spectra of insulating materials often involves slight deflection of the surface. Hence, the spectrum presented in figure 4.6(a) is that of TiO_{2-x} and not perfect rutile. Intensity measurements of the O:1s and Ti:2p regions of corresponding core level spectra indicate that $x \leq 0.1$.

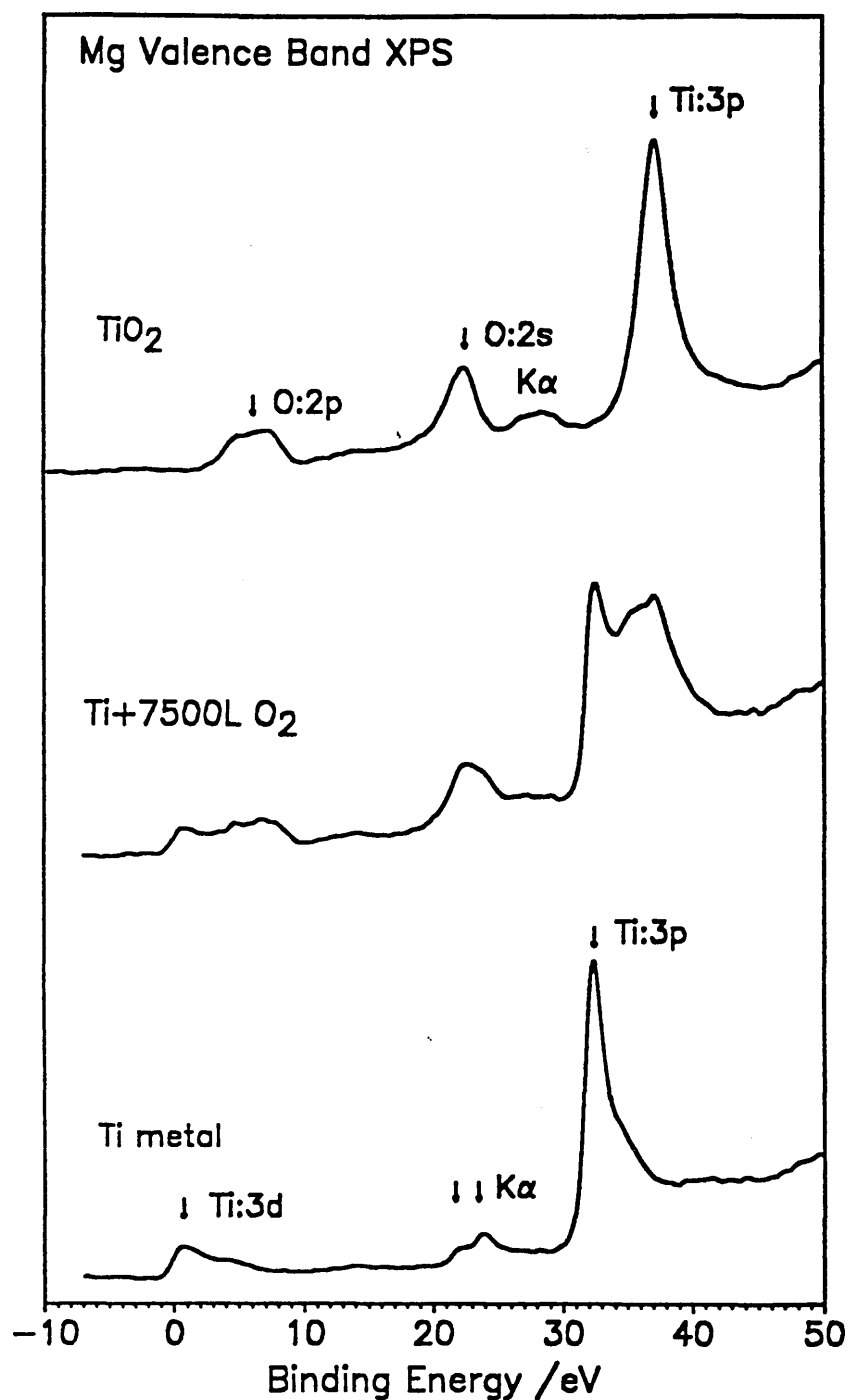


Figure 4.6: Valence band spectra ($h\nu=1253.6\text{eV}$) of (top) slightly defective $\text{TiO}_2(110)$ (middle) clean polycrystalline Ti foil exposed to 7500L O_2 and (bottom) clean Ti foil. Oxidation is accompanied by a decrease in Ti:3d intensity at E_F , an increase in O:2s and O:2p features and the appearance of chemically shifted Ti:3p structure attributable to a TiO_2 -like oxide.

The spectrum of clean Ti shows the presence of Ti:3d states centered just below the Fermi level. The Ti:3p peak is located at a binding energy of 32.3eV, shifted -5.0eV with respect to rutile. Some structure is visible to the high binding energy side of the metallic 3p peak which is due to the oxygen adsorption. Some weak O:2p structure is visible at 3-7eV but unfortunately, overlap of Ti:3p satellites and the O:2s peak means that it cannot be easily quantified. Nevertheless, the growth of both O related features was observed during spectral measurement.

Turning to the spectrum of polycrystalline Ti exposed to 7500L O₂, features associated with both metallic Ti and TiO₂ are observed. The surface is metallic as indicated by a measurable 3d intensity at E_F. Again, overlapping O:2s and Ti:3p x-ray satellite structure is observed, together with poorly separated O:2p states centered around 6eV binding energy.

Figure 4.7 shows the Ti:3p region of oxidised Ti. Analogous to the chemical shifts seen in the 2p region, structure shifted +5.0eV binding energy with respect to Ti metal, is visible. Clearly, this can be associated with Ti⁴⁺ of rutile. Furthermore, the region between these features is complex, and the difference data suggests the presence of other Ti species.

4.6 A Consideration of Previous Work

Although the interaction of the Ti surface with O₂ has been the subject of many investigations by a variety of experimental techniques, confusing and sometimes contradictory conclusions were reached by different authors. It has been claimed that TiO^{4.5, 4.6, 4.7}, Ti₂O₃^{4.8} and TiO₂^{4.9, 4.10, 4.11} is the oxidation product of Ti. General disagreement about the thickness of the overlayer at different exposures has further complicated matters. Nevertheless, the use of XPS has been invaluable in this respect since Ti²⁺, Ti³⁺ and Ti⁴⁺ are distinguishable by changes in Ti:2p and 3p binding energies.

The surface of TiO₂ and defected TiO₂ have been studied by a variety of workers using contemporary surface science techniques. Several studies have shown that there are no electronic states in the bandgap of perfect rutile^{4.12, 4.13, 4.14, 4.15}. Bandgap states can be introduced by ion or electron

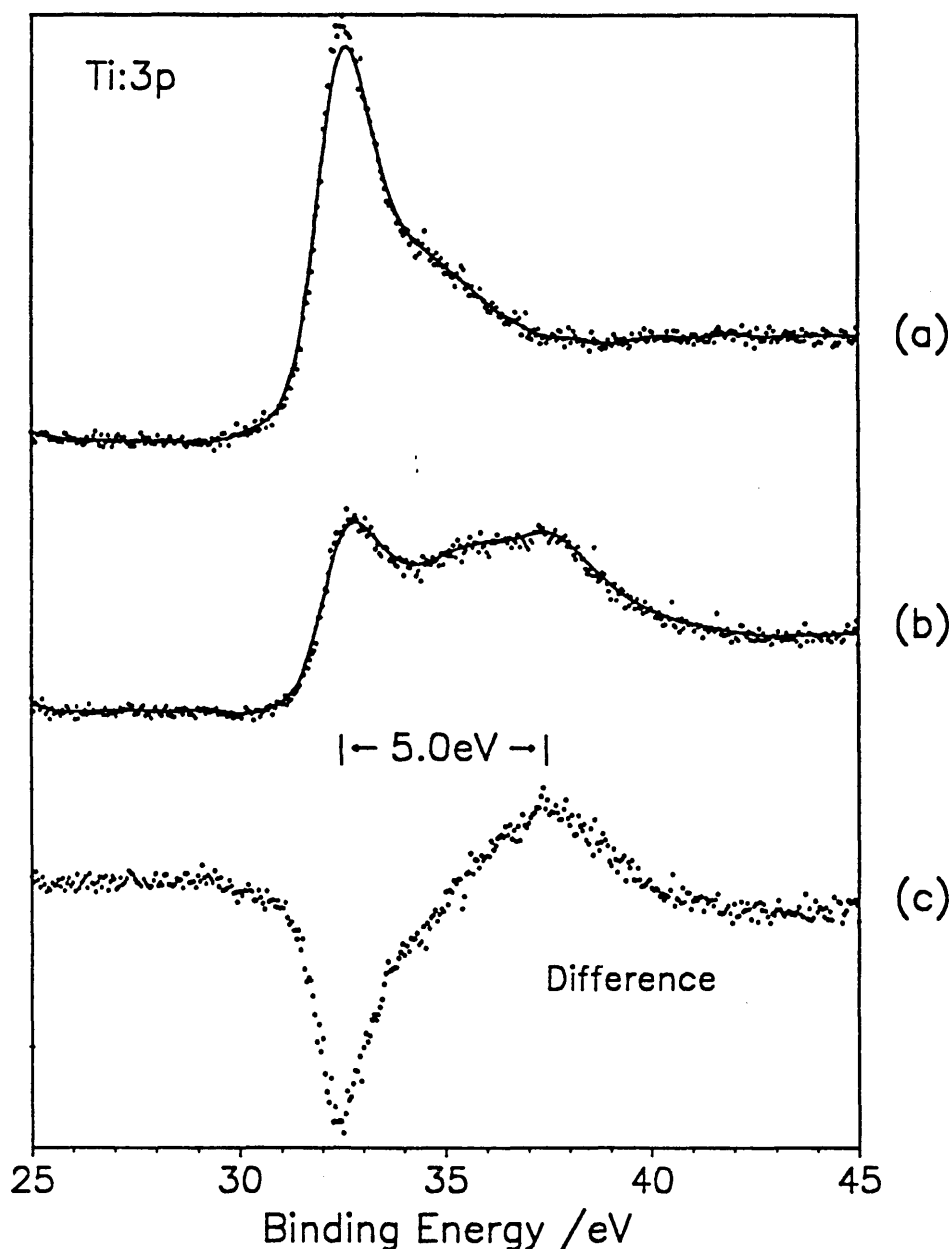


Figure 4.7: Detail from figure 4.6 of (top) the Ti:3p spectra of clean Ti foil (middle) Ti foil exposed to 7500L O₂ and (c) difference data (oxygen exposed minus clean). Similar to the difference data of the 2p region (figure 4.4), structure chemically shifted to 5.0eV higher binding energy appears upon oxidation, but smaller intensity changes are apparent extending down to the initial peak. The high binding energy shoulder observed in the spectrum of clean Ti is due to some oxidation of the clean Ti surface during spectral accumulation.

bombardment or heat treatment^{4.16, 4.17} and shown diagrammatically in figure 4.8. The presence of these states causes the rutile surface to become grey-blue in colour. Surface defects on $\text{TiO}_2(110)$ were examined in part by XPS in studies by Göpel *et al*^{4.4, 4.18}. Both the Ti:2p and 3p peaks exhibit increased spectral weight at 1.7eV lower binding energy upon moderate defection. More severe bombardment results in the appearance of distinct structure shifted by 3.1eV to lower binding energy and broadening of O:1s intensity. Identical chemical shifts were measured in the Ti:2p and 3p regions. It was concluded that increasing defection of the rutile surface generates first Ti^{3+} , then Ti^{2+} species at the surface. Very severe bombardment can generate Ti metal.

Armstrong and Quinn^{4.19} examined the surfaces of electrochemically oxidised (H_2SO_4 , KClO_4 and HClO_4) Ti films by AES and XPS. All partially oxidised Ti films presented complex Ti:2p XPS and LMV AES spectra. An examination of standard Ti materials, Ti, TiO , Ti_2O_3 and TiO_2 , was performed to determine the XPS binding energies of each of the various Ti:2p peaks. As a consequence, peak fitting of the oxidised spectra was possible and in all cases, electrochemically and atmospherically oxidised Ti films showed the presence of multiple oxidation states. It was not until very severe electrochemically oxidising conditions, that a sufficiently thick TiO_2 overlayer was formed to exclude XPS or AES signal from other sub-oxide species.

Analysis of TiO_2 -based electrode surfaces after a variety of treatments has also been undertaken by Armstrong^{4.20}. Again, by reference to the XPS spectra of standard Ti materials, the binding energies of Ti oxides were deduced, and complex 2p spectra subsequently curve fitted. Reduction of the film surface was performed by sputtering or by chemical reduction in H_2 .

The Ti sesquioxide, Ti_2O_3 , has a corundum crystal structure and is a semiconductor at room temperature^{4.21}. The presence of a large number of distinct phases between the stoichiometry of TiO_2 and Ti_2O_3 (the Magneli phases, $\text{Ti}_n\text{O}_{(2n-1)}$) focussed attention on the relation between defective TiO_2 and Ti_2O_3 .

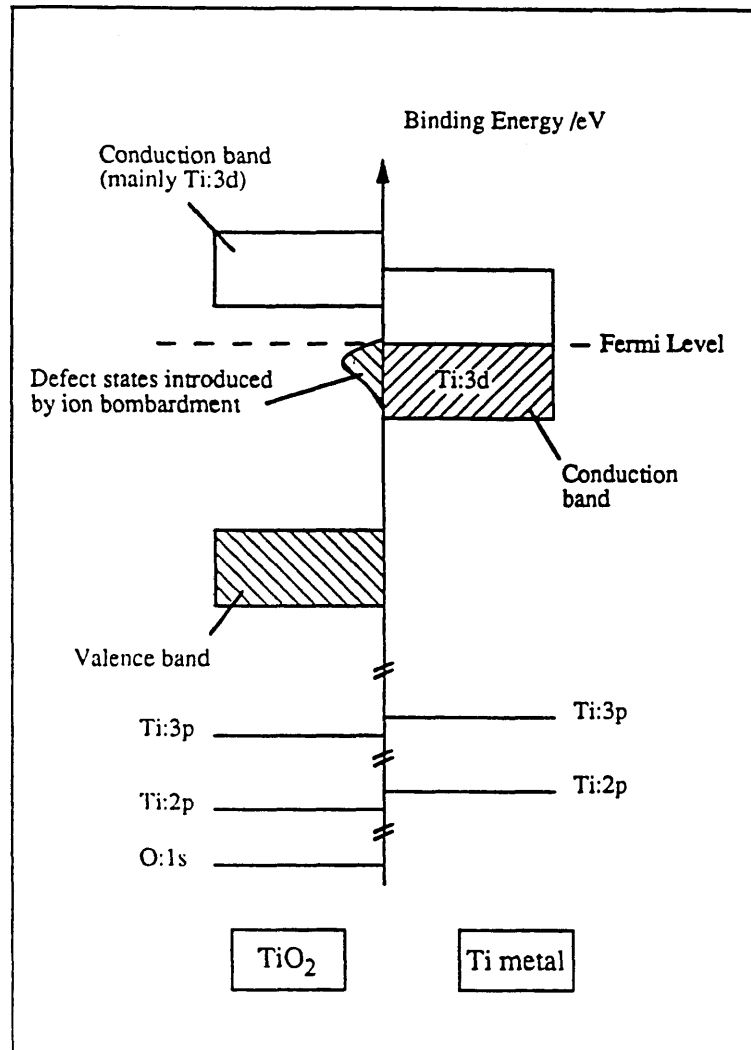


Figure 4.8: Band picture diagram illustrating the position of Ti^{3+} :3d defect states introduced by electron or ion bombardment of a perfect TiO_2 surface.

Ti₂O₃ has been studied by XPS and exhibits a complex Ti:2p shape, apparently due to the presence of a pair of superimposed doublets. The surface before cleaning showed features due to a thick TiO₂ overlayer^{4.22}. Reduction to Ti₂O₃ was achieved by heating *in vacuo* for 30 minutes at $\approx 870\text{K}$. These prepared surfaces showed very much broader Ti:2p peaks than either TiO₂ or Ti metal. Measurements on a cleaved Ti₂O₃ (047) surface^{4.23} confirmed that this is indeed the true XPS spectrum of Ti₂O₃. The broadening is a result of interaction between the core hole and the Ti:3d band. Ti₂O₃ has a d¹ configuration and at room temperature the occupied Ti:3d a_{1g} orbitals are separated from the unoccupied e_g orbitals by a band-gap of $\approx 0.1\text{eV}$ ^{4.24, 4.25}. Creation of a core hole in Ti₂O₃ pulls a_{1g} 3d levels out of the conduction band, leading to the formation of a localised state below the main d-band on the ionised atom. There are now two possible final states: either with this localised state occupied or unoccupied. If the state is filled, the core hole is 'screened' and the final state is Ti³⁺-like. However, if the level remains empty, an unscreened Ti⁴⁺-like final state results. Both final states contribute to the XPS spectrum.

A thorough study of the interaction of O₂ with the Ti metal surface by XPS was recently undertaken by Carley *et al*^{4.26}. Making extensive use of spectral subtraction techniques, the growth of Ti²⁺ (0 $\rightarrow$ $\approx 20\text{L O}_2$) and Ti³⁺ was observed at low exposures (<70L O₂), followed by appearance and eventual dominance of Ti⁴⁺ species at higher exposures (>100L O₂). The intensities of peaks due to suboxides reached a plateau after 100L exposure. After exposures of >100L, clear intensity growth at the low binding energy side of the original 2p_{1/2} peak was obvious. This is associated with the 2p_{3/2} multiplet shifted 5.3eV and due to oxidation to Ti⁴⁺. The binding energy values of Ti⁰:2p_{3/2} at 453.8eV and Ti⁴⁺:2p_{3/2} at 459.0 $\pm$ 0.1eV found here for clean Ti foil and TiO₂ respectively are in good agreement with those measured by Carley *et al* although there is no mention of the spectrometer binding energy calibration. The magnitude of the spin-orbit splitting (BE 2p_{1/2}-2p_{3/2}) found here as 6.2eV $\pm$ 0.1eV for Ti metal and 5.8eV $\pm$ 0.1eV for TiO₂ are also comparable.

A summary of the Ti:2p and Ti:3p binding energies determined by a number of authors is given in table 4.1.

Table 4.1: Ti:2p_{3/2} binding energies for Ti oxides /eV

Ti	TiO	Ti ₂ O ₃	TiO ₂	Ref
453.9	455.3	457.5	459.0	4.26
453.8	454.8		458.7	4.27
453.4	455.3		458.8	4.28
453.9			458.8	4.29
453.1	455.1	456.7	458.6	4.30
453.9		457.6	459.3	4.31
	455.7		459.1	4.32
453.9			459.0	This work

Ti:3p binding energies for Ti oxides /eV

32.3	37.3	This work
32.7		4.33
32.7	37.4	4.34

4.7 Peak Fitting of Ti:2p Structure

Some quantitative measurement of the concentration of various suboxide components of a particular Ti surface requires curve fitting of a complex 2p envelope. Without prior knowledge, the position and shape of constituent suboxide peaks can be greatly varied so there can be a large number of possible spectral fits. However, an examination of pertinent literature suggests limits of peak variability (position and shape) and so allows a reasonable attempt at fitting data to be made.

Satisfactory fits to the experimentally measured Ti:2p region of clean Ti metal and perfect TiO₂ were obtained by using a 70% Lorentzian/30% Gaussian peak shape, varying the peak height, width and asymmetry parameters as appropriate. Using these Ti⁰ and Ti⁴⁺ peak parameters, attempts at fitting more complex Ti:2p data was made. The width of the Ti³⁺ peak was increased relative to the other species in an attempt to crudely represent the experimentally observed broadened peak shape of Ti₂O₃ as discussed above.

Figure 4.9(a) shows the Mg K α XPS Ti:2p_{3/2} peak shape of a TiO₂(110) surface following bombardment with 2keV He⁺ ions for 40 minutes, after the subtraction of inelastic background. An attempt to generate the 2p envelope by the superposition of three peaks, representing Ti²⁺, Ti³⁺ and Ti⁴⁺ species, is also shown. Suboxide peak binding energies were based on those of Carley *et al.*^{4.26}. The Ti²⁺ and Ti³⁺ peaks were synthesised using the same parameters as the Ti⁴⁺ peak, but varying the peak height, width and asymmetry. Such a curve fitting routine shows that reduction of the rutile surface has occurred, generating Ti³⁺ and a small concentration of Ti²⁺ defect sites. Further ion bombardment causes growth of the Ti²⁺ peak and the gradual appearance of structure at 453.8eV due to metallic Ti⁴⁺.

The Ti:2p_{3/2} region of Ti metal exposed to 7500L O₂ is shown in figure 4.9(b). Again, the synthesised spectrum, also shown, is composed of four overlapping peaks. The Ti⁰, Ti²⁺, Ti³⁺ and Ti⁴⁺ peaks were all generated using the same set of parameters as those used to fit Ti, TiO₂ and the defective TiO₂ data in figure 4.9(a). The Ti⁰:2p_{1/2} at 460eV is included to improve the correlation in this region. This generated spectrum is further

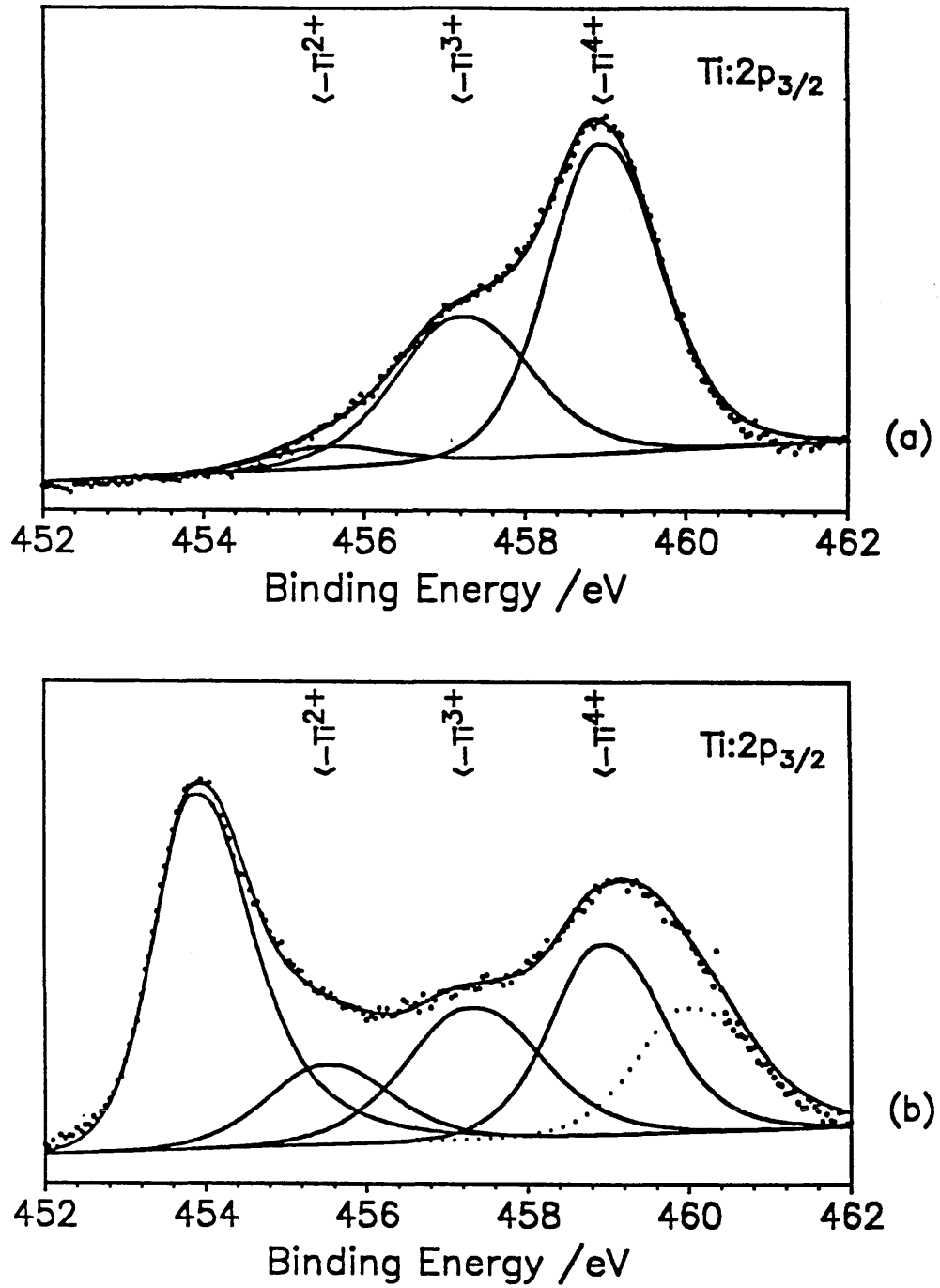


Figure 4.9: Ti:2p_{3/2} region of (a) rutile after defection by 2keV He⁺ bombardment for 40 minutes and (b) clean Ti foil exposed to 7500L O₂. In both cases the experimental data points are shown as heavy dots and synthesised peaks corresponding to Ti²⁺, Ti³⁺ and Ti⁴⁺ species, as solid lines. In (b) the light dots represent the synthesised 2p_{1/2}.

support for the existence of the three sub-oxide species on the moderately oxidised Ti surface. At the higher exposures, the Ti^{4+} peak becomes the most intense.

4.8 Hydrogen Contamination on the Ti(0001) Surface

Although an XPS contaminant-free Ti surface, could be easily generated, HREELS of the Ti single crystal surface showed the presence of a strong loss feature at 120meV as shown in figure 4.10(a). Such a feature has previously been observed on the clean Ti surface and attributed to Si contaminant on the basis of AES spectra^{4.35}. However, the difficulty of removing H from Ti has been well-documented^{4.36, 4.37} and so suggests this peak relates to Ti-H stretch modes on an H contaminated surface. To confirm this hypothesis, the crystal was exposed to D_2 at room temperature. A decrease in the loss intensity at 120meV was accompanied by an increase at 84meV as shown in figure 4.10. This is direct evidence that the feature at 120meV loss energy is in fact Ti-H related and that isotopic exchange occurs upon exposure to D_2 . Furthermore, it is possible to say that the H coverage of the as-prepared surface approximately corresponds to monolayer saturation since no further increase in total intensity occurs with D_2 exposure.

4.8.1 The Hydrogen Binding Site

It is possible to make some comment on the likely binding site of H on Ti(0001). The existence of only one, sharply defined vibrational mode is visible in the dipole scattering regime (specular direction) means that the site symmetry is C_{2v} or C_{3v} . The H atom is thus accommodated in either the on-top, the two fold hollow (bridging) or three fold hollow site. Theoretical studies of H interaction with transition metal surfaces^{4.38, 4.39} suggest that the site preference for H on Ti(0001) is the three fold hollow site on energetic grounds. Furthermore, studies using LEED and UPS to probe the Ti-H surface^{4.36, 4.41} demonstrated that theoretical modelling of DOS for various sites of H occupancy agree with experimental data if H is placed above the plane of the surface at this site. It was assumed that the first and second layer distance was unchanged from bulk Ti (unreconstructed) and that the Ti-H bond length was identical to TiH_2 (1.78Å). As such, calculations placed the H atom 0.42Å above the plane of the surface layer.

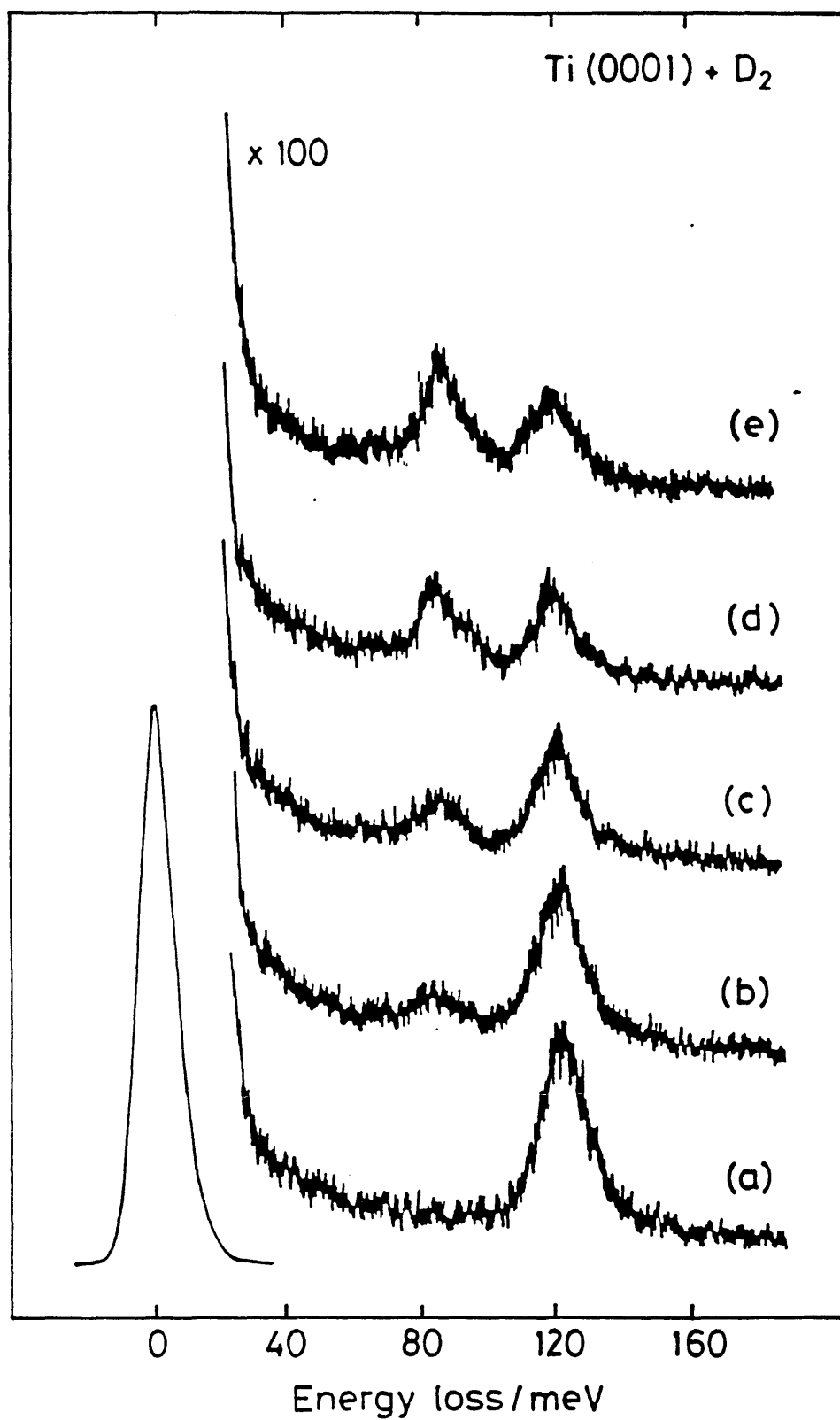


Figure 4.10: HREELS ($E_p=2.0\text{eV}$) of H contaminated Ti(0001) surface after exposure to D_2 at room temperature (a) 0L (b) 13L (c) 47L (d) 190L (e) 400L.

A feature at 125meV loss energy has been observed for H on TiC(111)^{4.42} which has the same hexagonal close packed surface structure as Ti and a very similar Ti-Ti spacing (3.06Å for TiC versus 2.95Å for Ti metal). No C-H bonding was observed in the HREELS of TiC, so the authors were confident in assigning the 125meV loss as a Ti-H stretch with H in the three fold hollow located 0.35Å above the surface plane based on impact scattering results. The geometry of this system is very close to that proposed above for the Ti/H system and so it is no surprise that the vibrational frequencies are so similar.

Early work by Sakamoto^{4.43} studied the optical vibrations of several transition metal hydrides by thermal neutron scattering. A series of hydrides $\text{TiH}_{1.3-2.0}$, gave identical (bulk) vibrational frequencies of 135meV (1090cm^{-1}) although this stoichiometry range spans a cubic-tetragonal phase transition.

In the present work, it was observed experimentally that the intensity of the 120meV feature decreased upon exposure to O_2 . Intensity was reduced by exposure to small doses of O_2 ($\approx 2\text{L}$) followed by a brief anneal at 600°C of $<60\text{s}$. However, the loss intensity in this region could not be eliminated entirely reflecting the tenacity of the hydrogen at the Ti surface. At the lowest hydrogen coverages, the Ti-H stretch region of the HREEL spectrum becomes broadened and may be indicative of two separate loss peaks, one at 120meV and one at 105meV as shown in figure 4.11(a). This is perhaps evidence of a second binding site, but the spectra are not sufficiently well resolved to comment upon this matter with any confidence. It is unlikely that this linked to the existence of two three-fold binding sites on a hexagonally packed substrate: with a second layer atom present or absent. Recently, the first experimental observations of these two binding sites by HREELS for H on f.c.c. Ni(111) have been made^{4.44} and in that case they are only 2.5meV apart.

Figure 4.11 shows this 'well-annealed' surface (with the minimum H contamination) exposed to H_2 at room temperature. It demonstrates that even after relatively high H_2 exposures, little change is observed in the Ti-H region at 100-120meV. The feature growing up at 65meV is due to oxygen

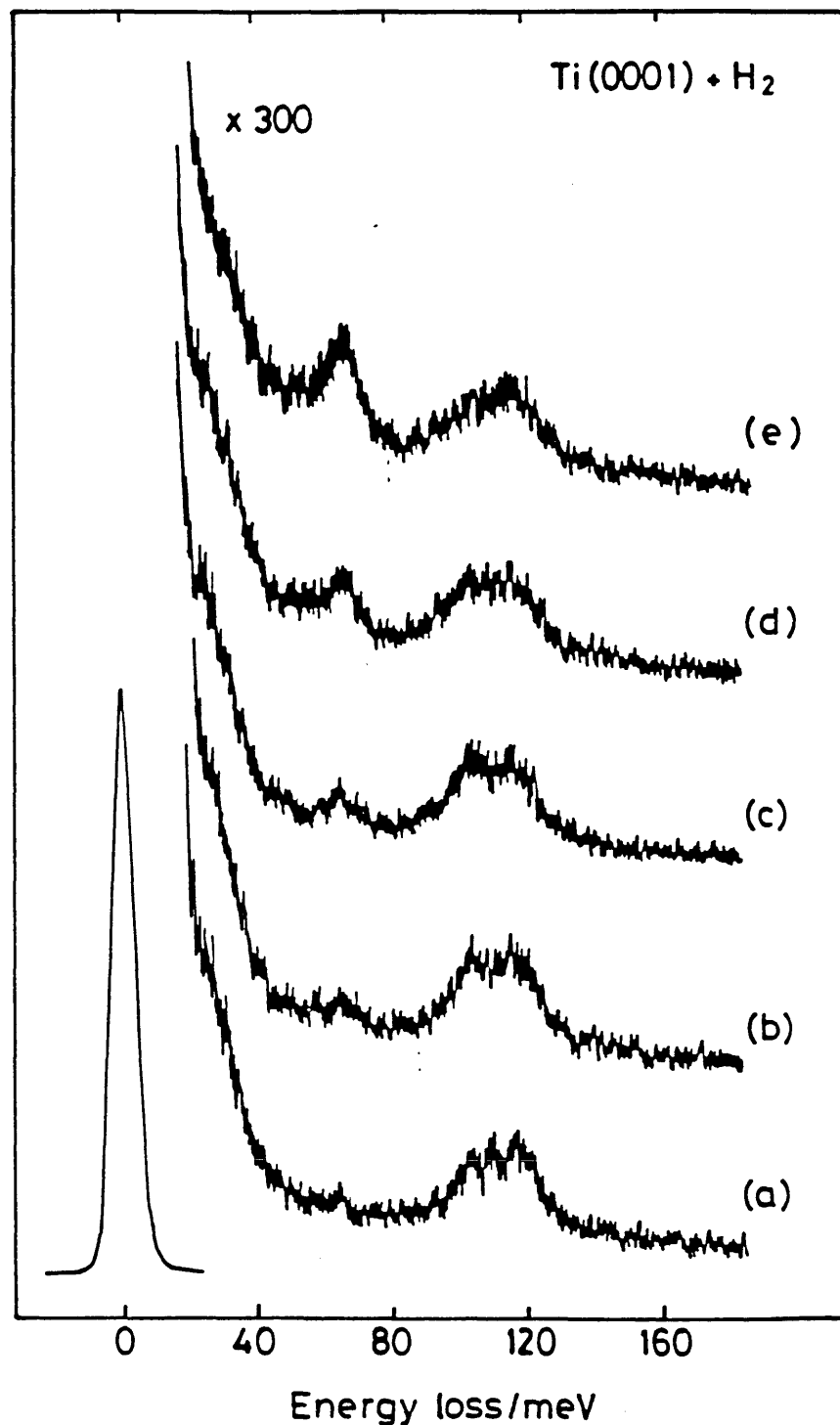


Figure 4.11: HREEL spectra ($E_P=2.0\text{eV}$) of (a) 'well-annealed' Ti(0001) surface showing some irreducible H contamination as a broad feature at 100-120meV. Exposure of this surface to H_2 at 300K results in little change in this region (b) 70L (c) 240L (d) 940L (e) 2700L. The loss peak at 65meV is due to O contamination during measurement.

adsorption during spectral accumulation. The failure to find increased intensity due to Ti-H bonding is rather surprising in view of the D_2 exposures mentioned above. It would appear that either the well-annealed Ti surface is relatively unreactive to H_2 , or that H diffuses into the bulk so quickly that negligible concentration remains at the surface.

4.9 The Oxidation of Ti(0001) Followed by HREELS

4.9.1 Small Oxygen Doses (<1L)

High resolution electron energy loss spectra ($E_p=2.0\text{eV}$) of the Ti(0001) surface taken after exposure to small doses of oxygen at room temperature are shown in figure 4.12. Before any exposure, the irreducible H content discussed above can be seen as an extended feature at 100-120meV. At very low exposures, a loss peak develops at 65meV and continues to grow up for exposure of less than 0.5L. Accompanying the growth of the 65meV peak, the Ti-H loss intensity is seen to decrease rapidly, although whether this is due to chemical displacement of the H atoms by O or screening of electron-dipole interactions in the presence of an adsorbate, is not clear. The growth of another loss peak at $\approx 42\text{meV}$ is also indicated.

The vibrational frequency of molecular O_2 corresponds to 193meV (1556cm^{-1})^{4,45}. No loss intensity is seen in this region in oxygen exposed Ti(0001). The origin of the 65meV peak must therefore be due to direct Ti-O bonding. The observed vibrational frequency is broadly in line with the frequencies observed for O in the three fold hollow site of other metal surfaces where the adsorption site has been determined by LEED as shown in table 4.2.

4.9.2 Evidence for Subsurface Oxygen

In dipole scattering, the sampling depth within a metal substrate is limited by the effective screening by conduction electrons of any time-dependent dipole established in the interior by an adsorbate. For typical metals, this screening length is of the order of $1\text{\AA}$ and so all subsurface dipoles are invisible except perhaps between the first and second atomic

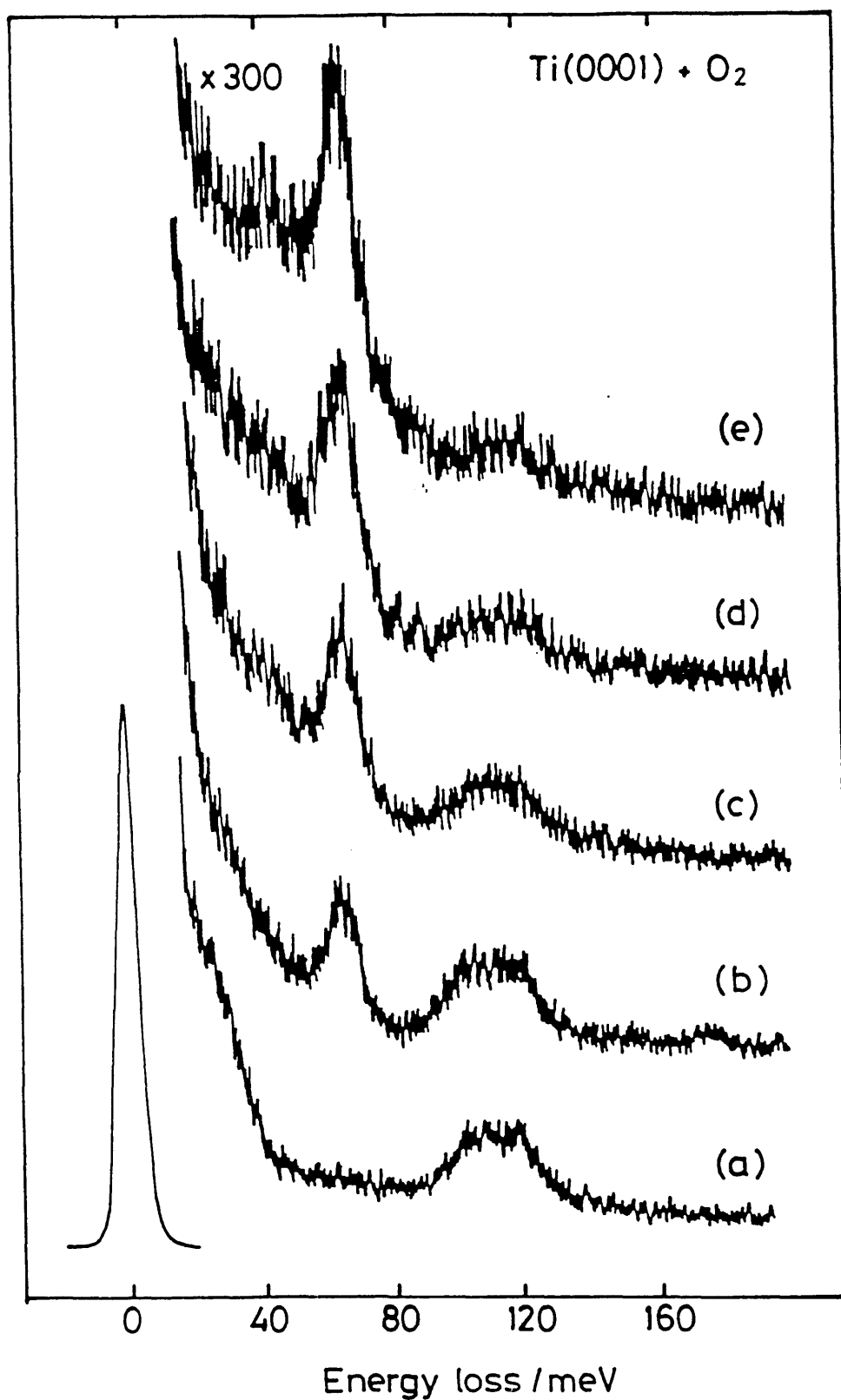


Figure 4.12: HREEL spectrum ($E_p=2.0\text{eV}$) of Ti(0001) surface exposed to O₂ at 300K (a) 0L (b) 0.02L (c) 0.06L (d) 0.25L (e) 0.5L. Note the growth of a feature at 42meV loss energy.

Table 4.2: Vibrational frequencies for O and H at three fold hollow sites on various substrates

	cm ⁻¹	meV	Ref
H + TiC(111)	1010	125	4.42
H + Ni(111)	1120	139	4.46
	800	99	4.47 [§]
O + Ni(111)	580	72	4.48
O + Ru(111)	515	64	4.49
O + Pt(100)	490	61	4.50 [¶]

§ There is evidence that this is associated with subsurface H vibrations in the Ni lattice.

¶ Reconstructed

layers^{4.51}. It is therefore tempting to assign the 42meV peak as due to subsurface O, probably between the first and second layers. This idea is supported by the gradual fading of the LEED pattern shown in figure 4.13. The pattern remains 1x1 but spots become increasingly blurred and have disappeared by 1L exposure, indicative of major surface order disruption probable burying of the O atoms. Although both (1x1) (high exposure) and p(2x2) (low exposure) LEED patterns have been reported for the O/Ti system^{4.35}, it was not possible to observe either here.

The idea of subsurface O in the Ti lattice has been suggested by other authors to explain unusual features of the O/Ti system. Work by Stockbauer and Madey *et al*^{4.52, 4.53} on oxygen desorption from Ti(0001) surfaces by electron and photon stimulation showed the desorption rate experiences an onset after 1-2L O₂ exposure. Very small desorption cross-sections were implied for exposures below 2L. Furthermore, the work function of the surface initially decreases and then rises again after 1-2L exposure. UPS confirmed that there were at least two distinct adsorption forms for O on Ti(0001), the first characterised by very low desorption rates, negative-going work function and a UPS feature at -5.9eV. At exposures greater than 1L, the work function difference becomes positive-going, the desorption yield increases dramatically and additional features develop in the UPS spectra. It was suggested that the first form may correspond to subsurface oxygen.

Similarities between the oxidation of Al(111) and Ti(0001) provided the motivation for parallel studies of the two systems by Strong and Erskine^{4.35}. In the case of Al(111), they were able to fit experimental HREELS data (which is qualitatively very similar to Ti(0001)) to an over- and under-layer O atom in a three-fold hollow and octahedral hole respectively using previously determined lattice dynamical calculations. The data for O/Al(111) was interpreted as an 80meV loss corresponding to overlayer O in the three-fold hollow site with the additional features at 40-50meV due to subsurface O vibrations.

In recent studies, an ordered p(1x1)O overlayer on Fe(100) gave HREELS loss peaks at 53meV (425cm⁻¹) corresponding to O in the four fold hollow site as confirmed by calculations and by LEED and low energy ion scattering (LEIS). In addition, much weaker loss peaks at 35meV (280cm⁻¹)

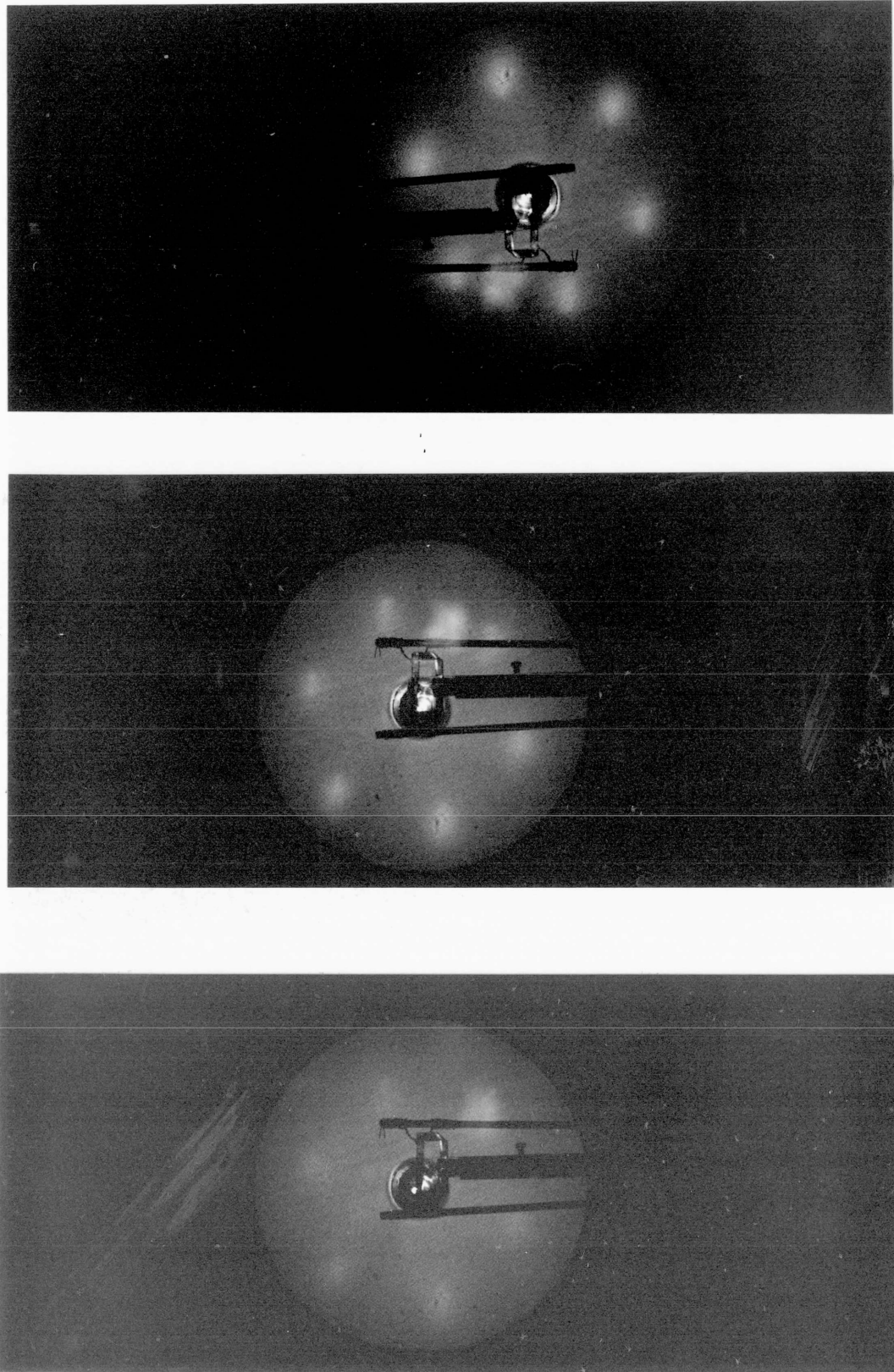


Figure 4.13: Fading of 1x1 hexagonal LEED pattern of Ti(0001) surface with oxygen exposure (a) clean (b) after 0.25L (c) after 0.55L O_2 . $E_p=89\text{eV}$.

were observed. It was suggested that this peak could be due to an α -Fe surface phonon, excited through enhanced dipole coupling through the ordered 1x1 overlayer^{4.54}. The c(2x2)N-Fe(100), c(2x2)C-Fe(100) and c(2x2)S-Fe(100) overlayers showed only a single loss peak^{4.55}. Similar surface phonon peaks have also been reported for p(2x2)O-Fe(100)^{4.56}, p(2x2)O-Ni(111)^{4.57}, p(2x2)O-Ni(100)^{4.58} and p(2x2)O-Ru(0001)^{4.59} and confirmation has been provided in some cases by lattice dynamical calculations.

It is therefore difficult to assign the origin of the 42meV loss peak unambiguously. It may be due to subsurface O vibrations, probably between the first and second layers. Alternatively, it may be that the peak is indeed due to formation of an ordered O overlayer on the Ti(0001) surface, enhancing dipole coupling to a Ti surface phonon as has been observed in other systems. The latter is not supported by the fading of the LEED pattern observed experimentally. No lattice dynamical calculations for Ti have been found.

4.9.3 Larger Oxygen Exposures

The HREEL spectra for an H contaminated Ti(0001) surface exposed to larger doses of O₂ at room temperature are shown in figures 4.14 and 4.15. Notice that after exposure of 0.5L O₂, this surface shows a broad, less well defined loss at 65meV than the comparable exposure on the well-annealed surface, figure 4.12(e), reflecting the degree of annealing. After an exposure of 1L the HREELS peak has broadened considerably and another loss centered at 85-90meV becomes clear. At the same time, the 1x1 LEED pattern disappears. No LEED pattern is visible at any higher oxygen exposure. Growth of both HREELS features continues with exposure, but by 30L (figure 4.15(b)) the high energy loss is strongest. At the highest exposures, a distinct loss feature at 65meV is no longer visible though there is strong loss intensity in this region (between 20 and 90meV). The 90meV loss continues to grow and shifts slightly upward in energy and is positioned at about 95meV after exposure to 17000L O₂.

The loss energy of the Ti-H and Ti-O related features (where a well-defined peak maximum is visible) are shown in figure 4.16 for each oxygen

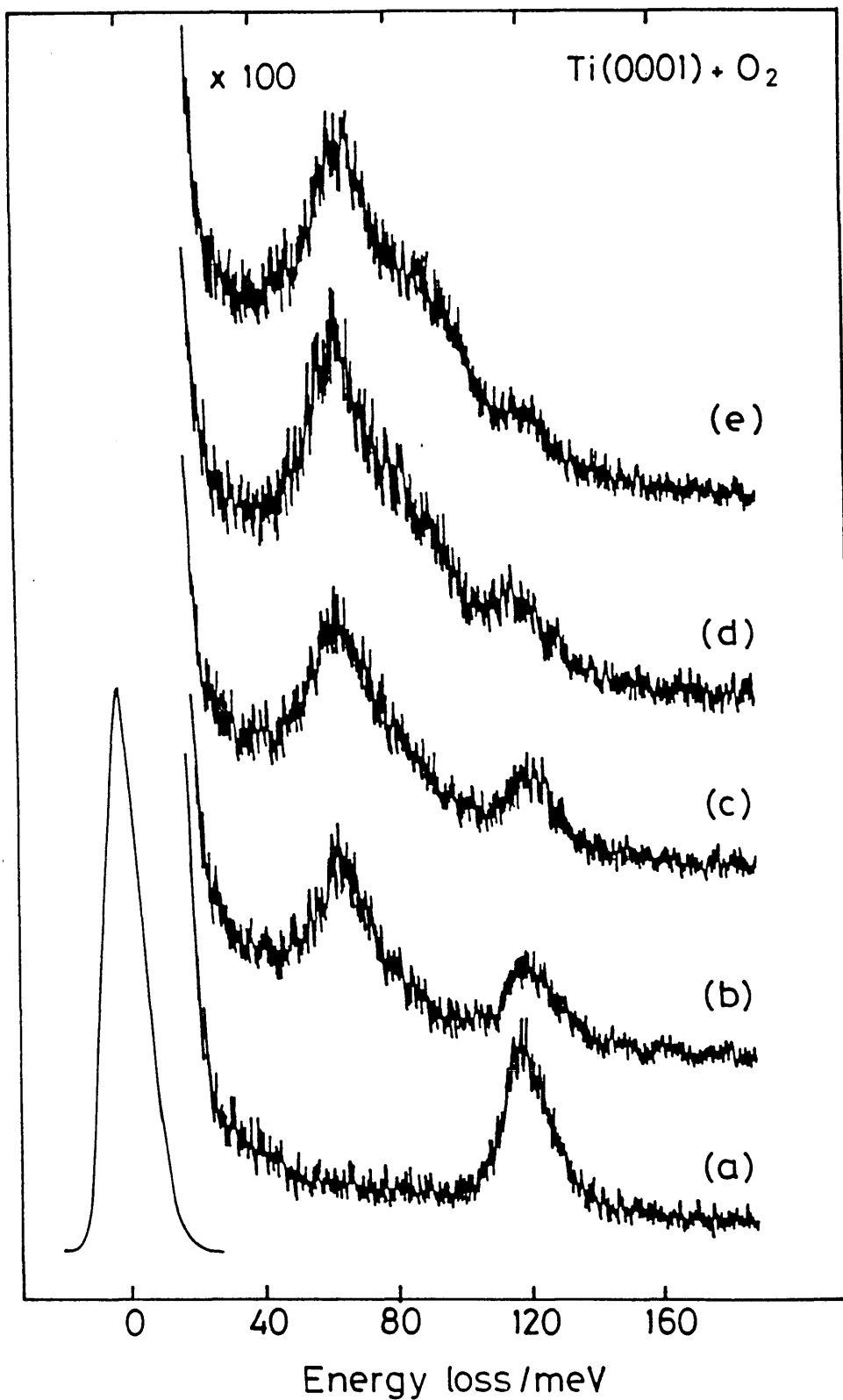


Figure 4.14: HREEL spectra ($E_p=2.0\text{eV}$) of the H contaminated $\text{Ti}(0001)$ surface with exposure to O_2 (a) 0L (b) 0.5L (c) 1L (d) 1.5L (e) 2.2L

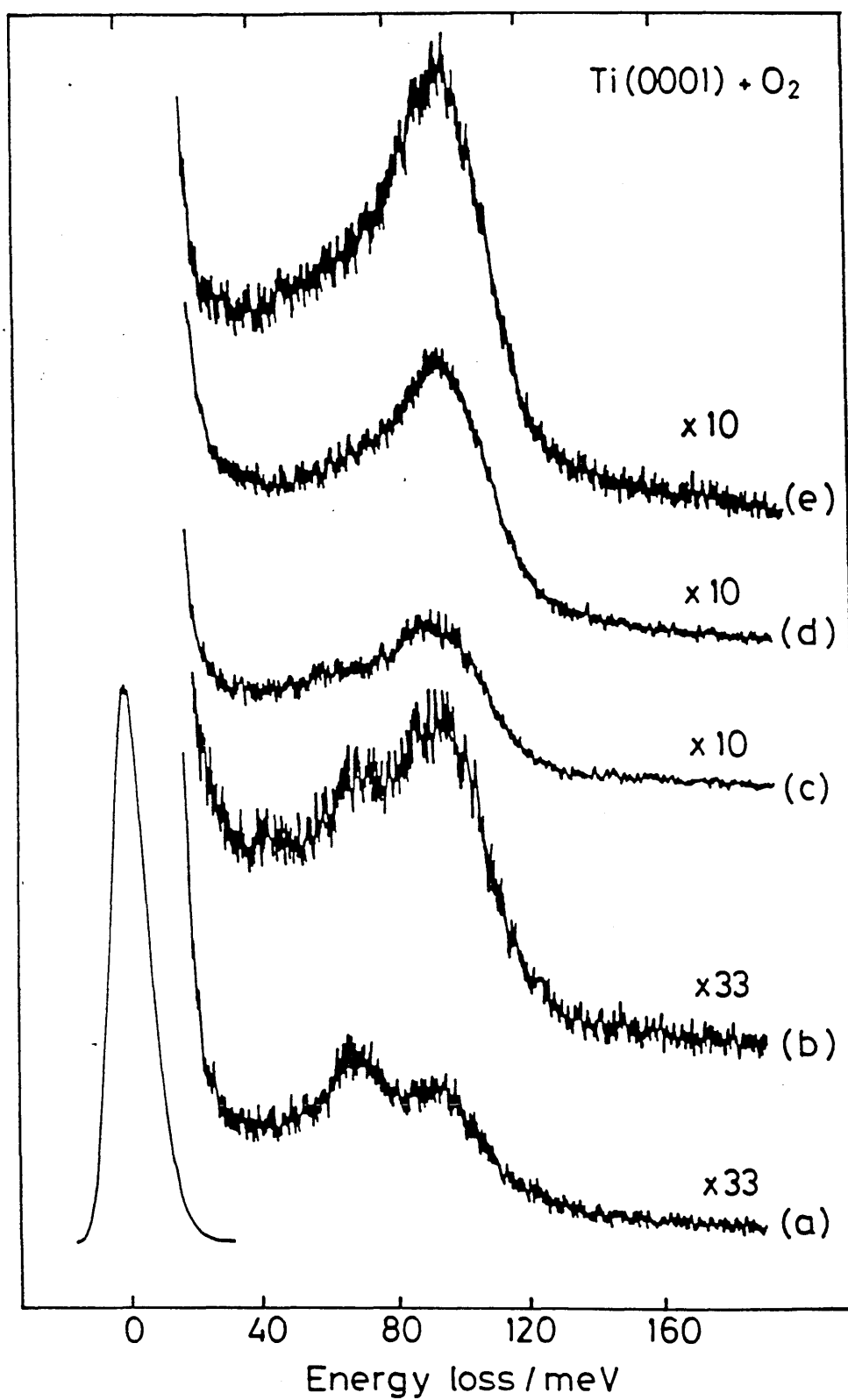


Figure 4.15: HREEL spectra measured with 2eV beam energy of the H contaminated Ti(0001) surface with exposure to O₂ (a) 7L (b) 30L (c) 250L (d) 3000L (e) 17000L.

exposure. Also shown is the integrated loss intensity at each exposure relative to the elastic peak intensity.

As has already been discussed, XPS points to the growth of a TiO_2 like surface oxide at high oxygen exposures. In this respect, it is interesting to compare the HREELS spectrum of $\text{TiO}_2(110)$ measured elsewhere^{4,3} and shown in figure 4.17, with that of oxidised Ti.

The limiting energy of 95meV found for the broad loss intensity induced by O on $\text{Ti}(0001)$ corresponds exactly with the highest surface optical phonon of rutile. However, even a cursory inspection of the oxidised Ti and TiO_2 spectra shows very little similarity in other respects. The perfect $\text{TiO}_2(110)$ surface shows three phonon modes associated with infra-red active displacements within the tetragonal unit cell. The energies of these phonons have been measured as 44, 52 and 94meV and are very intense. The spectrum also shows strong overtone features. It is known^{4,3, 4.60} that reduction of the TiO_2 surface, either by electron or ion bombardment, results in changes in the HREELS spectrum. In particular, the energy of the highest phonon mode in TiO_{2-x} is seen to shift *downward* in energy to 91meV when $x=0.12$ and 88meV when $x=0.18$. The shift is believed to be the result of a modified dielectric constant in the surface layer of defective TiO_2 . This is analogous behaviour to the *upward* shift in loss energy seen in the case of oxidation of Ti as observed here.

4.10 Conclusions

The chemical shifts seen in XPS data has demonstrated that the dominant oxidation product of a polycrystalline or single crystal Ti surface at room temperature after moderate oxygen exposure is a TiO_2 -like oxide. Furthermore, there is also evidence for substantial concentrations of both Ti^{2+} and Ti^{3+} oxides in this overlayer. Similar changes are seen in both the Ti:3p and 2p core level spectra. The valence band Ti:3d intensity (DOS at E_F) is observed to decrease in intensity with increasing oxidation consistent with decreasing metallic character.

The 1x1 LEED pattern of $\text{Ti}(0001)$ fades with very small oxygen exposures at room temperature, and has completely disappeared after

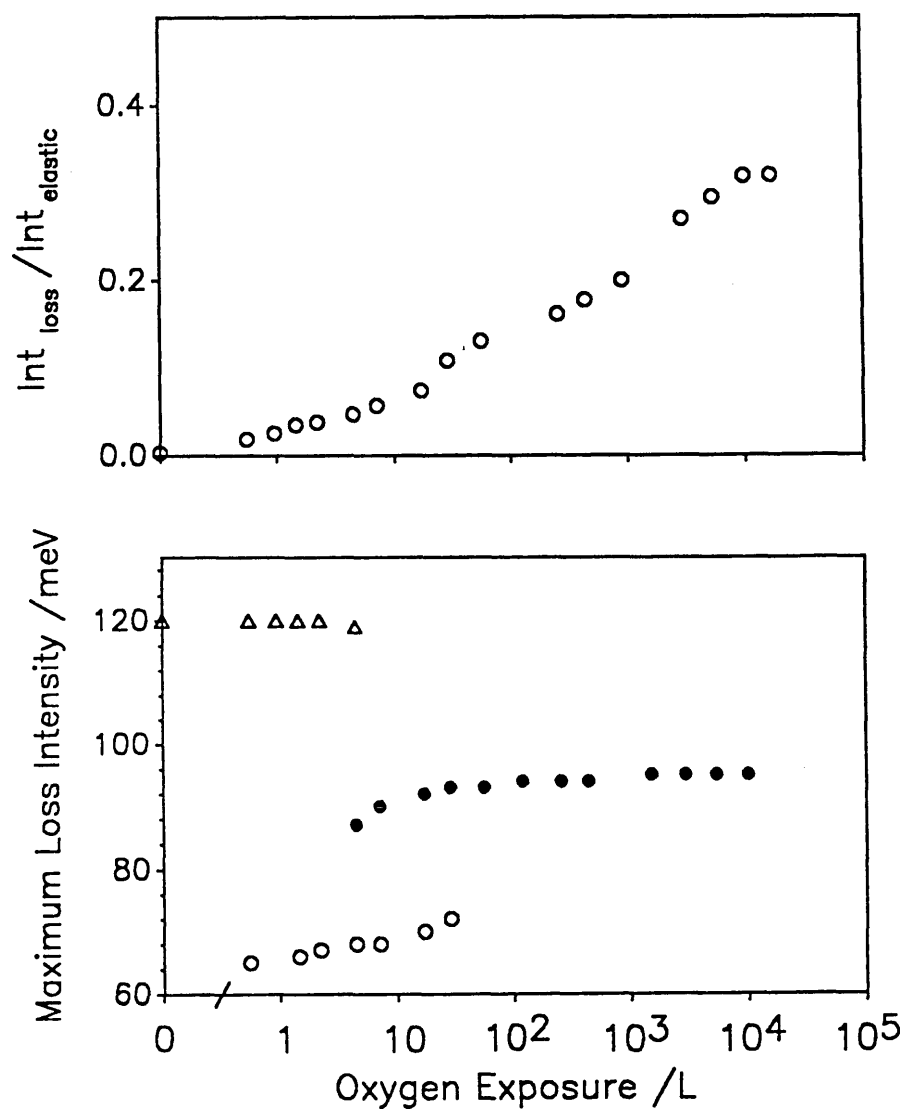


Figure 4.16: Top panel: The integrated HREELS loss intensity for Ti(0001) relative to elastic peak intensity with exposure to O_2 . Bottom panel: The loss energy of well defined peak maxima in HREELS spectra of H contaminated Ti(0001) with exposure to O_2 .

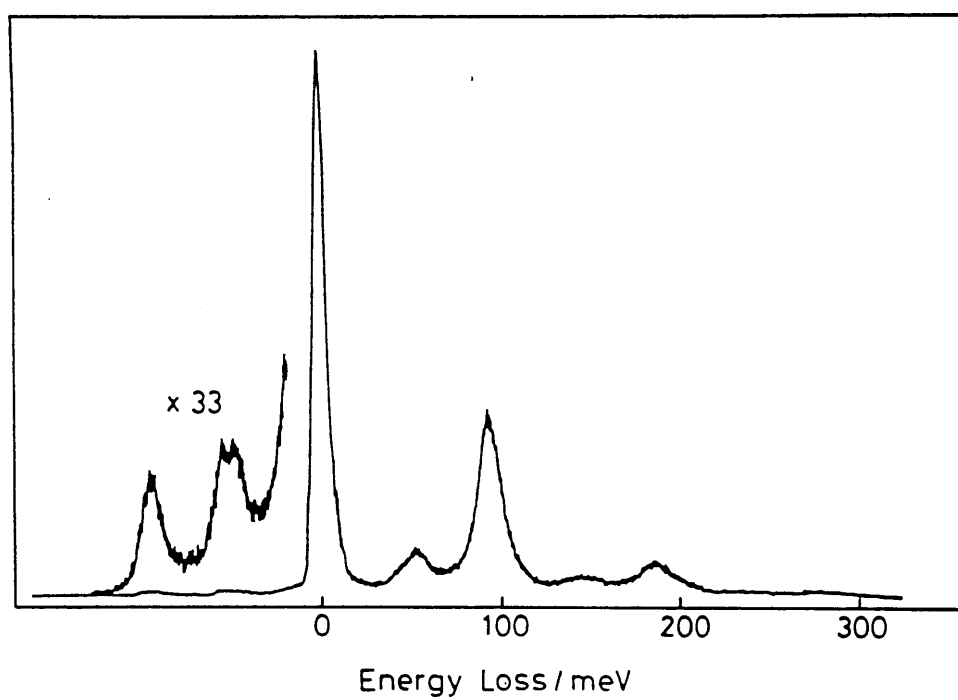


Figure 4.17: The HREEL spectrum of $\text{TiO}_2(110)$ measured with a beam energy of 7.0eV ^{4.60}. The losses are due to the excitation of optical phonons.

exposures $>1\text{L}$. This is indicative of major surface rearrangement and/or burying of O atoms into the Ti substrate. No ordered O overlayer was detected.

HREELS has identified a feature at 120meV loss energy due to Ti-H vibrations and confirmed by isotopic substitution. However, the reactivity of the $\text{Ti}(0001)$ surface towards H_2/D_2 appears to be linked to the degree of surface order. The reaction of O_2 with Ti produces different low and high exposure oxides. For exposures $<1\text{L}$, a strong loss peak at 65meV and a weaker one at 42meV is obvious. At higher exposures, a feature at 90meV begins to appear and shifts to 95meV at high exposure, dominating the HREELS spectrum.

The HREELS measurements indicate that a TiO_2 -like layer (probably oxygen deficient) forms at the surface of $\text{Ti}(0001)$ upon oxidation. The absence of well defined phonon structure, visible in single crystal $\text{TiO}_2(110)$, suggests the oxide layer on Ti metal possesses the short range Ti-O six fold co-ordination, but does not have the long range order of rutile.

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5. The Sputtering Behaviour of CoTi

Changes in the surface composition during sputtering and annealing are encountered in many compounds, including transition metal alloys^{5.1}. The alloy CoTi is no exception, and in this work compositional changes were observed with bombardment by Ar^+ ions and also with annealing at elevated temperatures.

5.1 The Polished CoTi Surface

The surface of CoTi single crystal, as obtained from the supplier, was polished with progressively finer diamond paste finishing with $1/4\mu$ grade, rinsed in propan-2-ol and finally washed in distilled water in an ultrasound bath as discussed in detail in chapter 3.

During preliminary work in the HREELS vacuum system, the polished CoTi surface was examined by XPS. Figure 5.1 shows the Mg XPS core level spectra of the Ti:2p, Co:2p, O:1s and C:1s regions of this surface prior to any *in situ* treatment. The broad Ti:2p_{3/2} peak is at $\approx 462\text{eV}$ and the O:1s at $\approx 534\text{eV}$ binding energy. There is a considerable C:1s doublet peak at 285eV and 288eV. Rather surprisingly, there is no detectable Co intensity.

If the Co:2p photoelectron pathlength is estimated at $8\text{\AA}$ ^{5.2} then the effective sampling depth of Co:2p photoelectrons is $\approx 35\text{\AA}$. Thus Co must be absent in the outer ≈ 10 atomic layers. Some Co:2p intensity does become visible at $\approx 778\text{eV}$ (2p_{3/2}) and 793eV (2p_{1/2}) after a short period of Ar^+ etching in the vacuum chamber as shown in figure 5.2. After sputtering, the Ti:2p_{3/2} peak occurs at 455.2eV, but some C and O contamination remains. The O:1s peak appears at 530.7eV and the C:1s intensity is reduced to just a single peak at 282eV.

The initially dominant C:1s peak at $\approx 285\text{eV}$ binding energy, removed preferentially with sputtering, is probably associated with weakly bound C-O/C-H species. Contamination due to hydrocarbon residues from diffusion pump oil also produces a C:1s peak at $\approx 285\text{eV}$ ^{5.3}. The minor component at $\approx 282\text{eV}$ is due to metal carbide species, and is more resistant to sputtering.

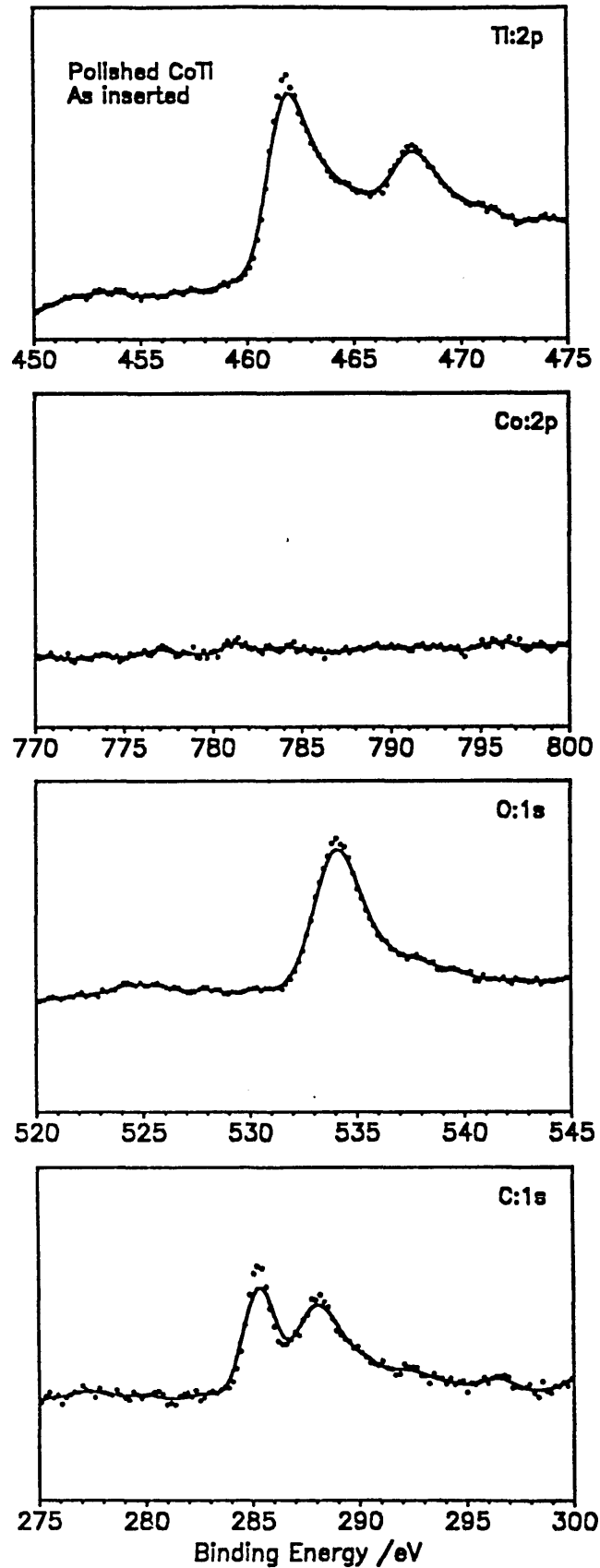


Figure 5.1: Mg XPS core level spectra measured in the Leybold-Heraeus system for polished CoTi prior to any *in vacuo* treatment. The higher than expected binding energies suggest an insulating surface.

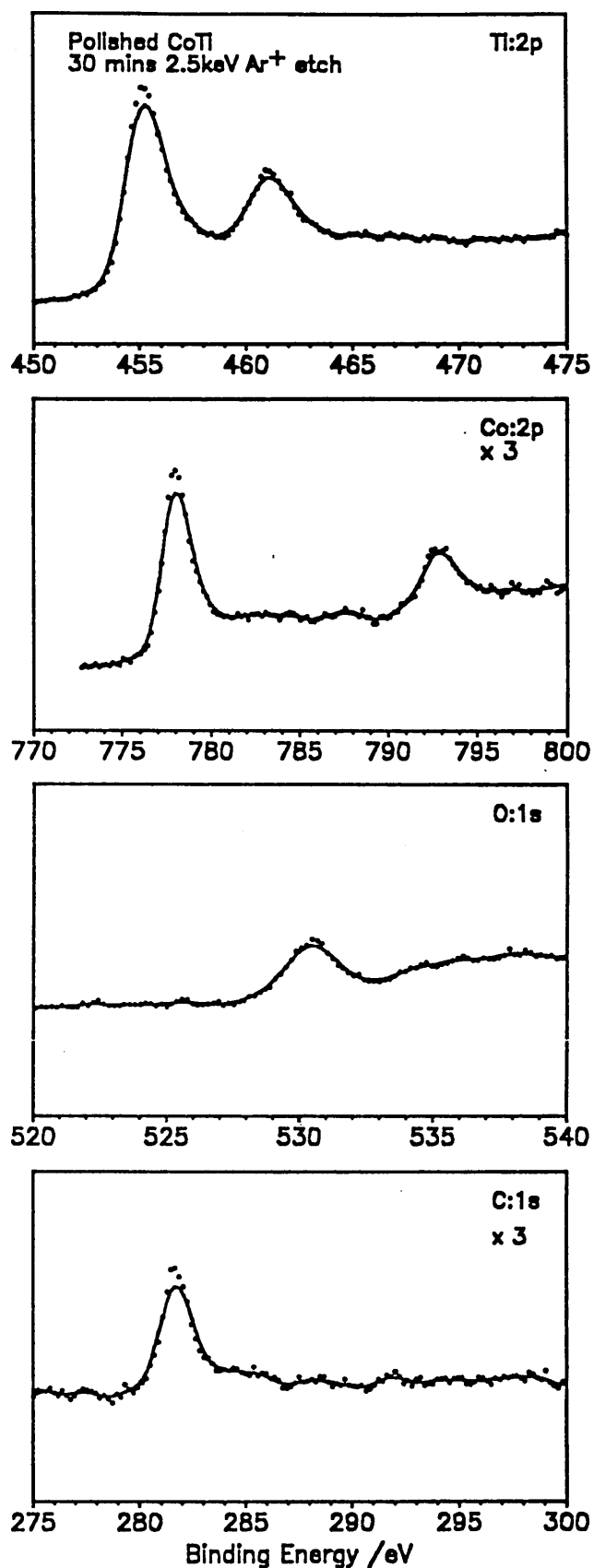


Figure 5.2: Mg XPS core level spectra for polished CoTi after sputtering with 2.5keV Ar⁺ ions for 30 minutes. Note the appearance of Co:2p structure.

Traces of C:1s structure at $\approx 282\text{eV}$ often remained, even with prolonged bombardment. Similar behaviour was noted in an investigation of carbide species on FeTi^{5.4} surfaces, where carbonaceous overlayers were removed easily by sputtering but some metal carbide remained. In particular, Ti is known to form both carbide species^{5.5} or oxycarbide species in the presence of an oxidised surface^{5.6}. Similarly, the O:1s structure with one peak at $\approx 530.5\text{eV}$ and one at 532.5eV , is associated with oxide and O-H/C-O contamination respectively.

Sputtering of the polished surface results in the appearance of Co:2p intensity which can be assigned to metallic Co by comparison with literature^{5.7, 5.8, 5.9, 5.10}. The Ti:2p_{3/2} peak at 455.2eV is nominally between that of Ti and TiO^{5.11, 5.12, 5.13, 5.14, 5.15} and this will be discussed in more detail later. The O:1s feature at 530.7eV and the C:1s peak at 282eV are reduced to just single peaks with sputtering, the positions of which are indicative of an oxide and carbide respectively.

Rivière has also commented on the absence of Co in the very top atomic layers of a mechanically polished CoTi single crystal during initial surface preparation as determined by AES measurements^{5.16}. In that work, the initial surface was composed of TiO₂ and C contamination. Extensive sputtering was necessary before the Co LMM Auger signal became visible and this was accompanied by reduction of the TiO₂ to metallic Ti and the removal of the initial carbon contamination. Some O remained, even after prolonged sputtering, concurrent with the work presented here.

5.2 Subsequent Atmospheric Exposure

Immediately following experimentation, the sputtered single crystal CoTi surface was exposed to a laboratory atmosphere for several weeks, and then inserted into the ESCALAB vacuum chamber without repolishing.

Figure 5.3 shows the Mg XPS spectra of the air exposed alloy surface measured in the ESCALAB. In this instance, Co:2p structure is immediately visible without any sputtering. Features in the Co:2p_{3/2} region are complex and characterised by a narrow peak at 778.3eV together with broader peaks at $\approx 782\text{eV}$ and $\approx 787\text{eV}$ binding energy. In the Ti:2p region,

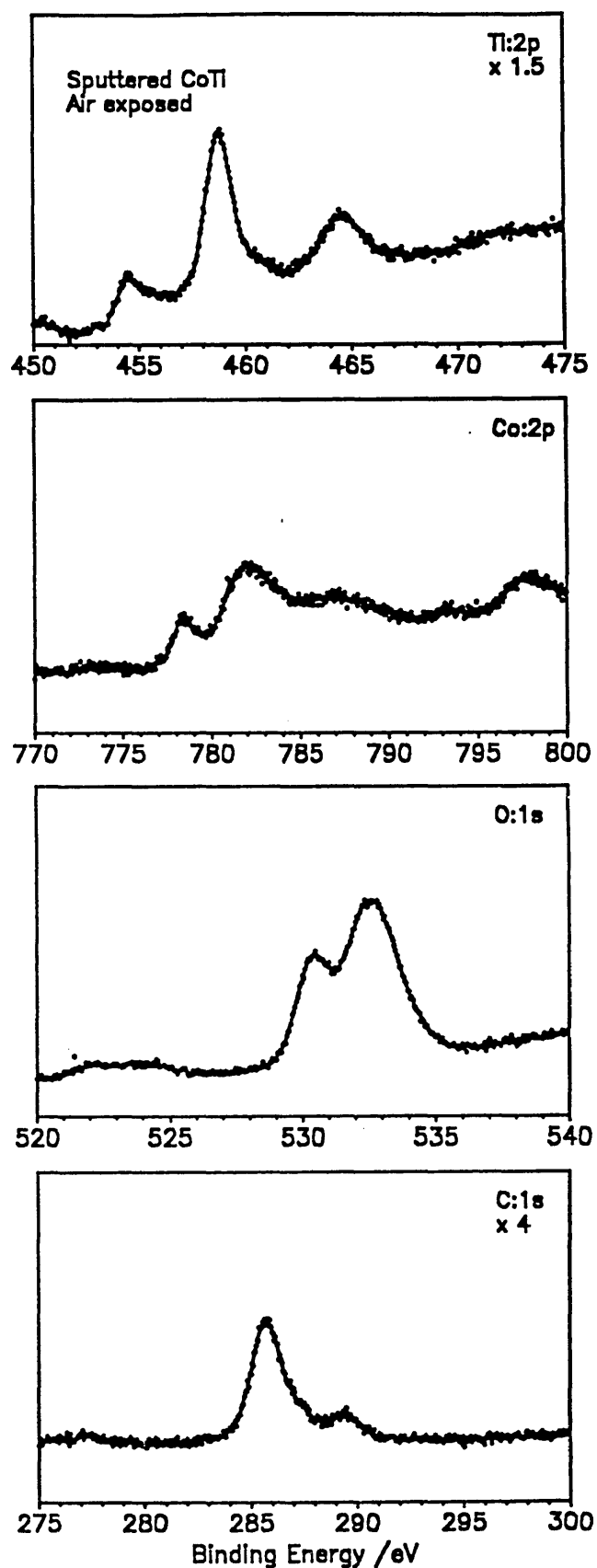


Figure 5.3: Mg XPS core level spectra taken in the ESCALAB system for a sputtered CoTi surface as inserted into the vacuum after exposure to air.

peaks at approximately 454.5eV, 458.8eV and 464.5eV binding energy can be attributed to a pair of superimposed spin-orbit split doublets due to Ti and TiO₂-like oxide^{5.11, 5.12, 5.13, 5.14, 5.15} as will be discussed in more detail in later chapters.

The O:1s core level again exhibits a double peak structure with one peak centered at 530.5eV and one at 532.5eV. The C:1s core level similarly has a twin-peak feature with the most intense peak at ≈ 285.5 eV binding energy. With subsequent sputtering of this surface, in both cases the higher binding energy peaks were removed preferentially leaving a single O:1s peak at ≈ 531 eV and a single C:1s peak at 282eV as before.

The core level features of the atmosphere exposed surface are consistent with the presence of C-H/C-O/O-H contamination, together with metallic Co and Co oxide and/or hydroxide species. The contamination must be the result of air exposure since no polishing was performed. The Ti:2p region shows the presence of TiO₂ together with a small concentration of metallic Ti in the alloy

Once a surface containing Co was prepared, re-exposure of the surface to air for periods of up to several months did not result in the absence of Co in the outermost layers. The obvious conclusion is that the phenomenon of total Ti segregation in the outer $\approx 35\text{\AA}$ relates to the polishing/cutting procedure adopted prior to *in situ* treatment.

5.3 Sputtering of CoTi Determined by AES

To study the sputtering of CoTi in further detail, the specimen was mounted (without repolishing) in the IPES chamber and sputtered by 500eV Ar⁺ ions at an incident angle of 20-25° from the surface normal. The range of 500eV Ar⁺ ions in a typical metal target has been estimated at $\approx 10\text{\AA}$ ^{5.17}. Spectra were measured in the N(E) mode and then converted to first derivative N'(E) spectra, allowing more accurate determination of peak position and peak-to-peak height. Peak assignments for Ti and Co are based on Coad *et al*^{5.18, 5.19} and are listed in table 5.1.

The N'(E) AES spectrum of the surface as inserted (before

Table 5.1: Auger electron energies compiled from literature^{5.18, 5.19}

Element	Assignment	Kinetic energy /eV [§]
S	L _{2,3} VV	150
Cl	L _{2,3} VV	180
C	KVV	<u>272</u>
Ti	L _{2,3} M ₁ M ₁	330
Ti	L _{2,3} M ₁ M _{2,3}	362
Ti	L _{2,3} M _{2,3} M _{2,3}	<u>382</u>
Ti	L _{2,3} M _{2,3} V	<u>416</u>
Ti	L _{2,3} VV	450
O	KL ₁ L ₁	472
O	KL ₁ V	490
O	KVV	<u>510</u>
Co	L ₃ M ₁ M _{2,3}	611
Co	L ₃ M _{2,3} M _{2,3}	651
Co	L ₃ M _{2,3} M _{4,5}	<u>713</u>
Co	L ₃ M _{4,5} M _{4,5}	<u>773</u>

[§] Energy of negative going peak in N'(E) mode

Underlining denotes strongest peaks.

sputtering) measured with 2keV electron beam energy is shown in figure 5.4(a). The expected Ti $L_3M_{23}M_{23}$ peak at 383eV and the $L_3M_{23}M_{45}$ (LMV) at 415eV are visible together with a weak Co $L_3M_{45}M_{45}$ peak at 773eV. However, the spectrum is dominated by intense C KVV and O KVV Auger peaks at 272 and 515eV respectively. It has already been mentioned above that the air exposed sample exhibited intense C and O XPS features. The peak at 175eV is due to Cl.

After 60s bombardment, as shown in figure 5.4(b), the Cl LVV is greatly reduced but the C KLL intensity has increased substantially relative to the O, Ti and Co signals indicating a C-rich subsurface region. After 120s bombardment, a feature at 215eV becomes visible but falls to negligible levels after prolonged bombardment. The energy of this peak closely corresponds with the quoted value for Ar embedded in Fe^{5.20}. Trapped Ar has also been observed on the FeTi surface^{5.21}. Levels of C and O were reduced gradually with sputtering but were not completely eliminated after 170 minutes sputtering as shown in figure 5.4(e). It was shown in extended experiments, that the C and O intensities could not be reduced below an irreducible level regardless of the sputtering duration.

The peak-to-peak heights of the features seen in the AES spectra of CoTi during sputtering are given in figure 5.5. A region of pronounced Co enrichment is observed after about 25 minutes sputtering. This coincides with a region of noticeable O depletion. The Cl signal falls to zero within the first 5 minutes of sputtering, but features due to C and O contamination do not reach minimum levels until ≈ 100 minutes of sputtering.

The sputtered surface shows enhanced Co and Ti Auger structure. Peaks due to the Co $L_3M_{23}M_{45}$ at 715eV and the Co $L_3M_{23}M_{23}$ transition at 653eV become visible and additional features in the Ti LMM are discernible. The $N(E)$ spectra for the as inserted and 170 minute sputtered surface, after subtraction of a linear sloping background, are shown in figure 5.6. The initial CoTi surface shows some S contamination at ≈ 145 eV not visible in the $N'(E)$ spectra.

Figure 5.7 shows the region of the Auger spectra dominated by Ti LMM transitions for the virgin and 170 minute sputtered surface. Both $N(E)$

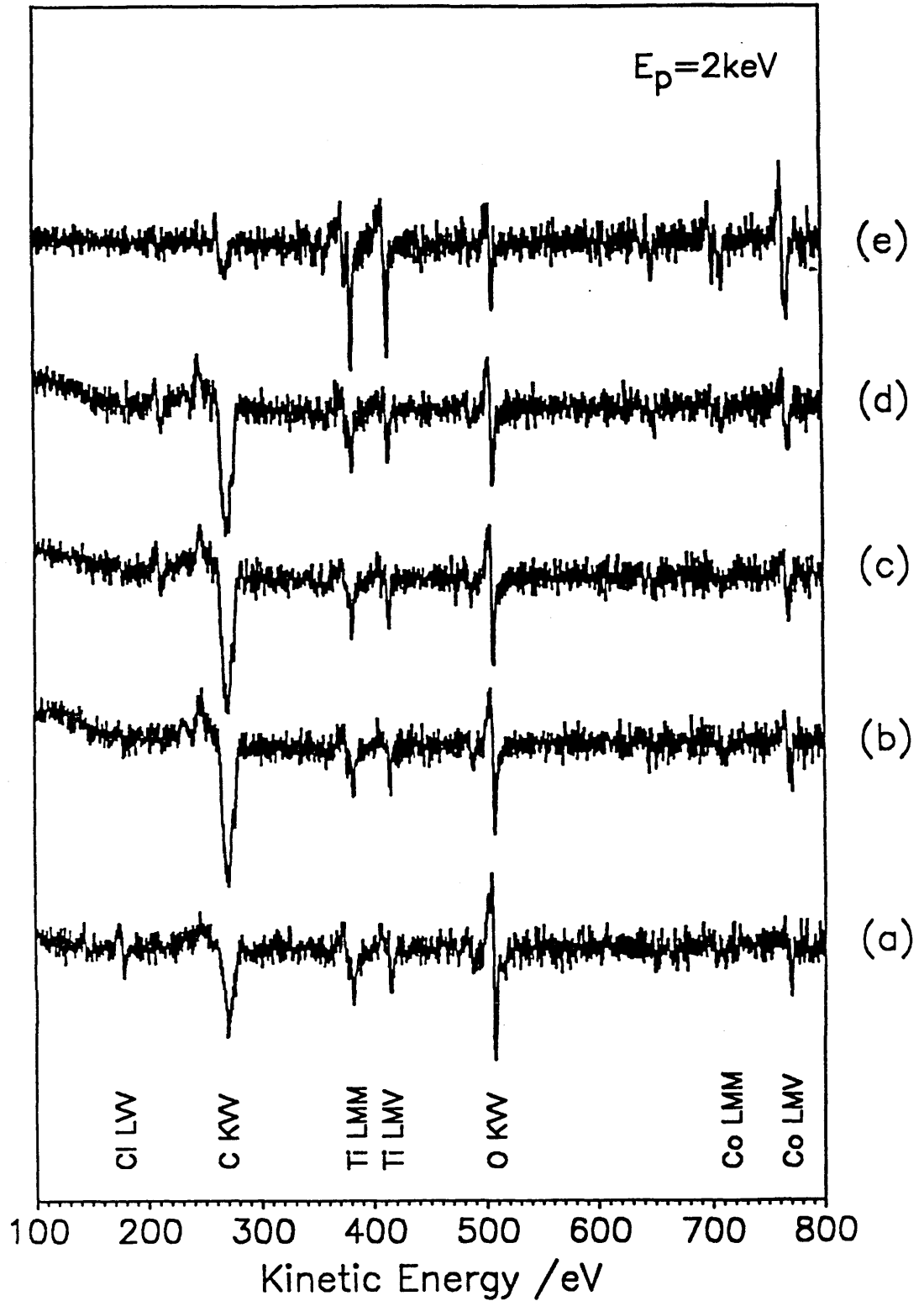


Figure 5.4: $N'(E)$ Auger spectra measured in the IPES system ($E_p=2\text{keV}$) for (a) a previously sputtered CoTi surface exposed to air and (b) after sputtering with 500eV Ar^+ ions for 60s (c) 120s (d) 180s (e) 170 minutes.

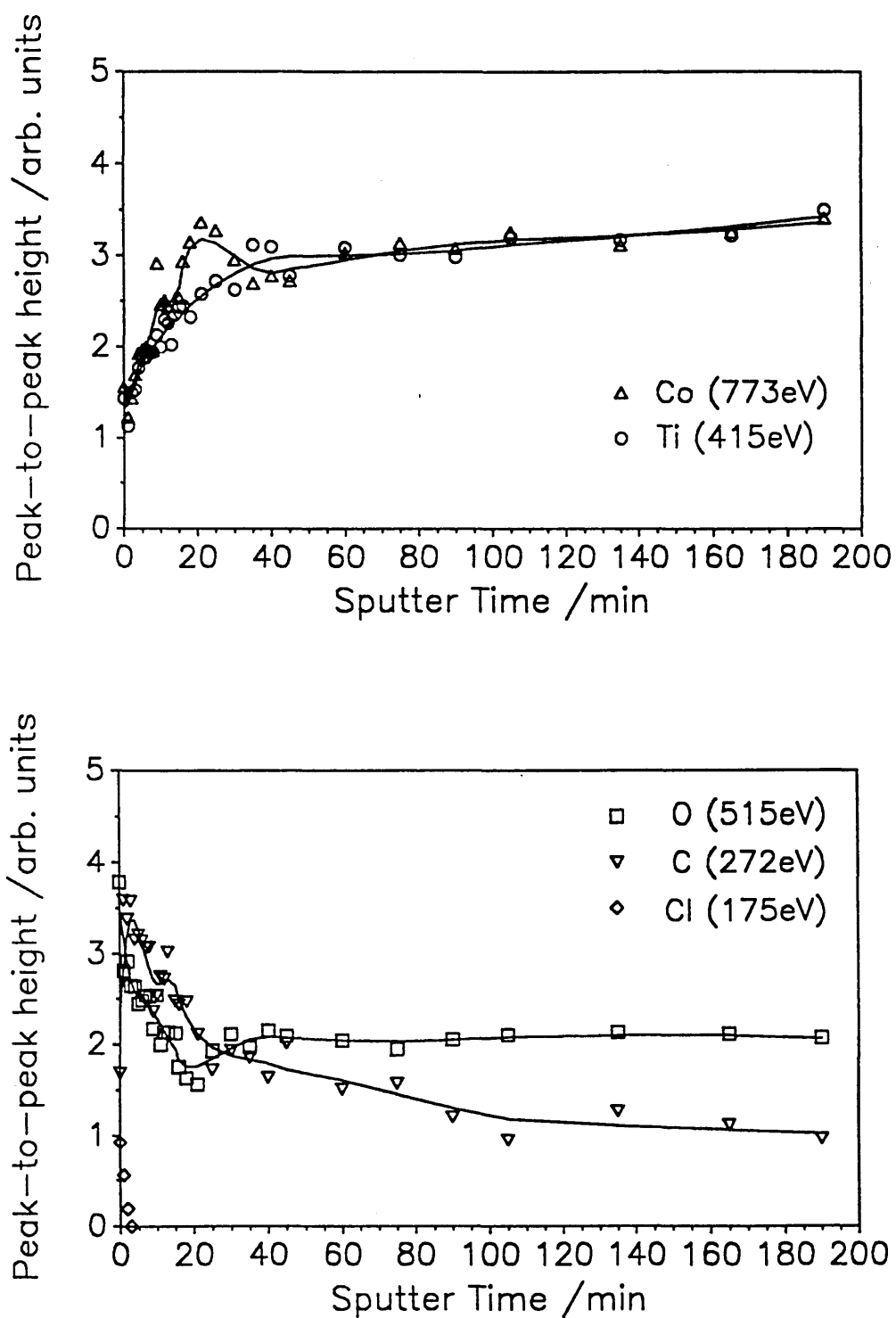


Figure 5.5: Peak-to-peak heights of Co (773eV), Ti (415eV), O (515eV), C (272eV) and Cl (175eV) Auger peaks in $N'(E)$ spectra with 500eV Ar^+ ion sputtering. Note the area of pronounced Co enrichment after 20 minutes.

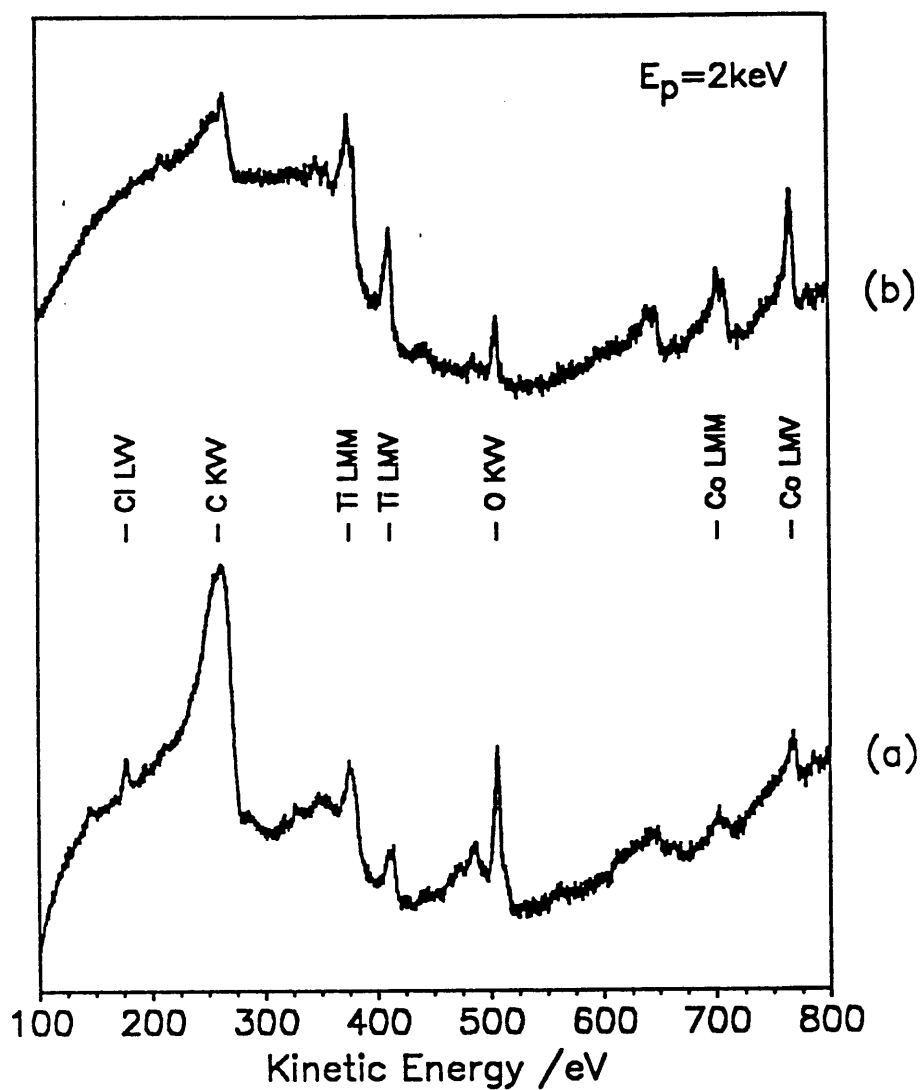


Figure 5.6: $N(E)$ AES spectra of (a) the sputtered CoTi surface exposed to air for several weeks and (b) after 170 minutes sputtering with 500eV Ar^+ ions. Note the reduction of the initially dominant C KVV and O KVV peaks. A straight-line background has been subtracted in both cases.

and $N'(E)$ spectra are displayed. Particularly noticeable are changes in the $L_3M_{23}M_{23}$ peak (383eV) and a narrowing of the $L_3M_{23}M_{45}$ (415eV) peak shape after sputtering. The 383eV peak becomes a distinct doublet with an additional feature at 376eV.

An examination of $N'(E)$ Auger spectra presented in the literature, as shown in figure 5.8, demonstrates that oxidation of Ti is accompanied by changes in Ti LMM peak shape. It has been shown that exposure to O_2 or electro-oxidising conditions^{5.22} results in the loss of the doublet peak in $N'(E)$ spectra at 383eV and a broadening of the 415eV peak, towards that of TiO_2 ^{5.23}. The doublet is characteristic of metallic Ti^{5.24}. The doublet is not present in $N'(E)$ spectra of TiO ^{5.25}. The presence of the doublet at 376/383, arrowed in figure 5.7, is evidence that the sputtered CoTi surface contains metallic Ti, although the presence of residual oxygen implies that oxidised Ti species may be involved. As was mentioned earlier, the AES spectra of Ti, TiO , Ti_2O_3 and TiO_2 are all very similar, and so AES cannot easily further distinguish the Ti oxide present.

5.4 The Effect of Incident Ion Energy

The composition of the CoTi surface was also followed by XPS in the ESCALAB UHV system after sputtering by Ar^+ with a range of initial kinetic energies. The surface was initially bombarded with high energy ions until irreducible of contaminant levels.

The sample was returned to the preparation chamber for a further etch at a particular ion kinetic energy[¶]. The surface was analysed by Mg XPS after 10 and 15 minutes sputtering to confirm that steady-state conditions had been reached and that surface stoichiometry was not changed by further bombardment. Care was taken to ensure that the sample remained in the same sputtering orientation throughout. A series of incident ion energies, starting at 8keV and gradually reducing to 2keV, was performed. To confirm that the changes in sample stoichiometry measured by this method were not an artefact of sample inhomogeneity, the series was repeated starting at 2keV

[¶] Although sample current cannot be measured directly in the ESCALAB system during bombardment, operation of an identical gun under identical conditions in the HREELS spectrometer gave a sample current of $4.5\mu Acm^{-2}$ at 3keV

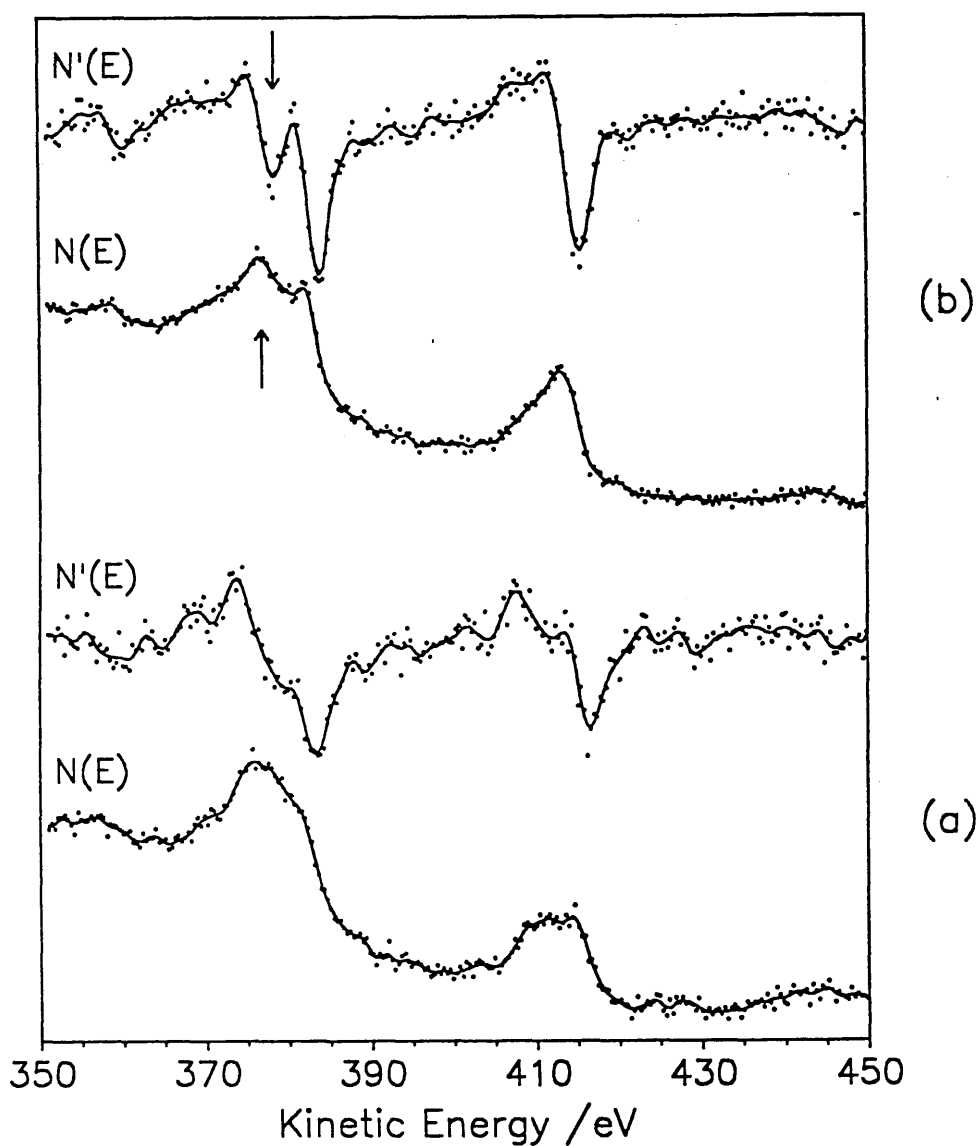


Figure 5.7: $N(E)$ and $N'(E)$ AES spectra of the Ti LMM region of (a) the sputtered CoTi surface exposed to air for several weeks and (b) after 170 minutes sputtering with 500 eV Ar^+ ions. Changes in the $L_{2,3}M_{2,3}V$ (415 eV) and the $L_{2,3}M_{2,3}M_{2,3}$ (370–380 eV) peak shapes occur due to the reduction of TiO_2 -like oxides to Ti caused by sputtering. Reduction is accompanied by the formation of a doublet peak at ≈ 375 eV.

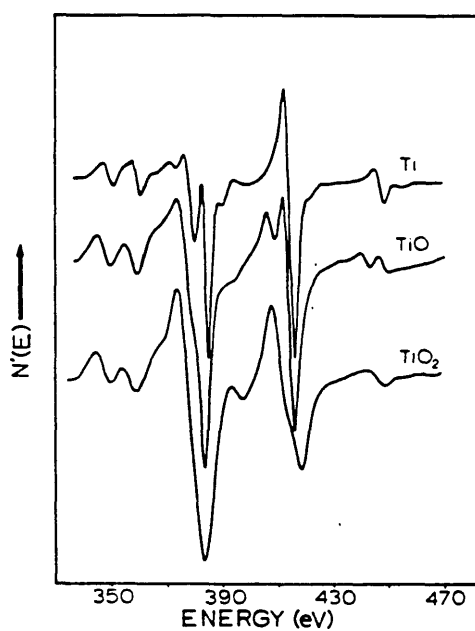
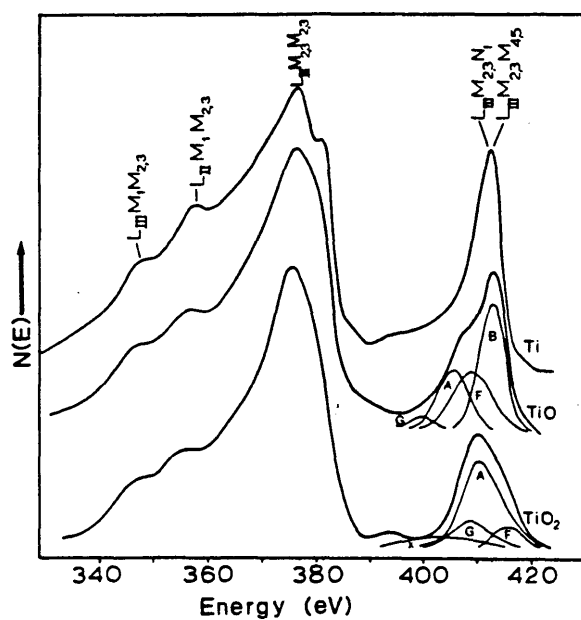


Figure 5.8: $N(E)$ and derivative $N'(E)$ AES spectra of Ti, TiO and TiO₂^{5.25}.

and gradually increasing the ion energy to 8keV.

The Co:Ti ratio during sputtering is shown in figure 5.9, after correction by suitable XPS sensitivity factors. After etching with 8keV Ar⁺ ions, the Co:Ti ratio reaches 1.46, indicating substantial enrichment of the Co component at the surface. As the ion energy is reduced, so the Co:Ti ratio falls until it reaches 1.22 after 2keV etching, still representing some degree of Co enrichment. This value compares favourably with the value of 1.17 obtained by Netzer *et al*^{5,26} after sputtering CoTi with 2keV Ar ions and the value of 1.18 obtained here by AES after sputtering with 0.5keV ions (above).

The O:Ti ratio is also shown in the figure, and exhibits a marked decrease with decreasing ion energy towards a minimum value of ≈ 0.3 at 2keV. There is little difference between the decreasing and increasing ion energy series of experiments.

5.5 Annealing Behaviour

Some of the damage created by the ion bombardment process can be removed by heating the sample. In this way, increased atomic mobility destroys some of the lattice defects created by bombardment and allows more rapid out-diffusion of embedded noble gas atoms. Unfortunately, annealing may also cause surface compositional changes: in this case, the segregation of Ti and associated O atoms.

The changes in the Co:Ti ratio induced by annealing, measured in the HREELS system, are shown in figure 5.10. The height of the Co LMV Auger versus the Ti:2p_{3/2} height is shown plotted for four annealing temperatures. These two peaks occur within 30eV in the Mg XPS spectrum and so effective sampling depths are very similar. The height ratio can be calibrated by measuring the corresponding intensity of the Co:2p peak and making corrections for electron pathlengths. Hence, a Co LMV:Ti:2p_{3/2} height ratio of 1.45 corresponds with 1:1 Co:Ti stoichiometry. The differences in initial stoichiometry reflect different sputtering energies during preparation. Spectra from samples annealed at 570 and 440°C were initially sputtered by 4keV Ar⁺ ions, whilst those taken on samples annealed at 370 and 660°C by 3keV Ar⁺ ions. The figure shows a decrease in the Co:Ti ratio

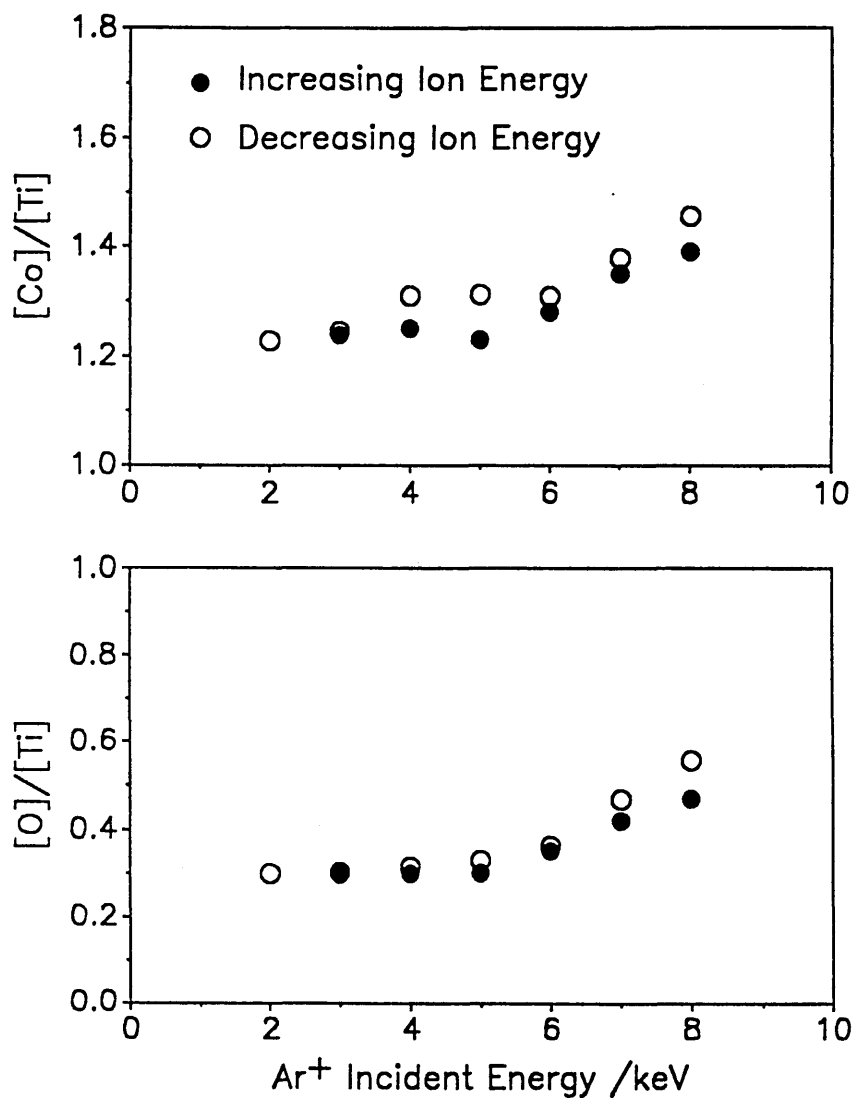


Figure 5.9: Change in Co:Ti and O:Ti surface ratios (corrected for sensitivity factors) of CoTi as a result of sputtering with Ar⁺ ions of 2-8keV. The decreasing energy series was performed first.

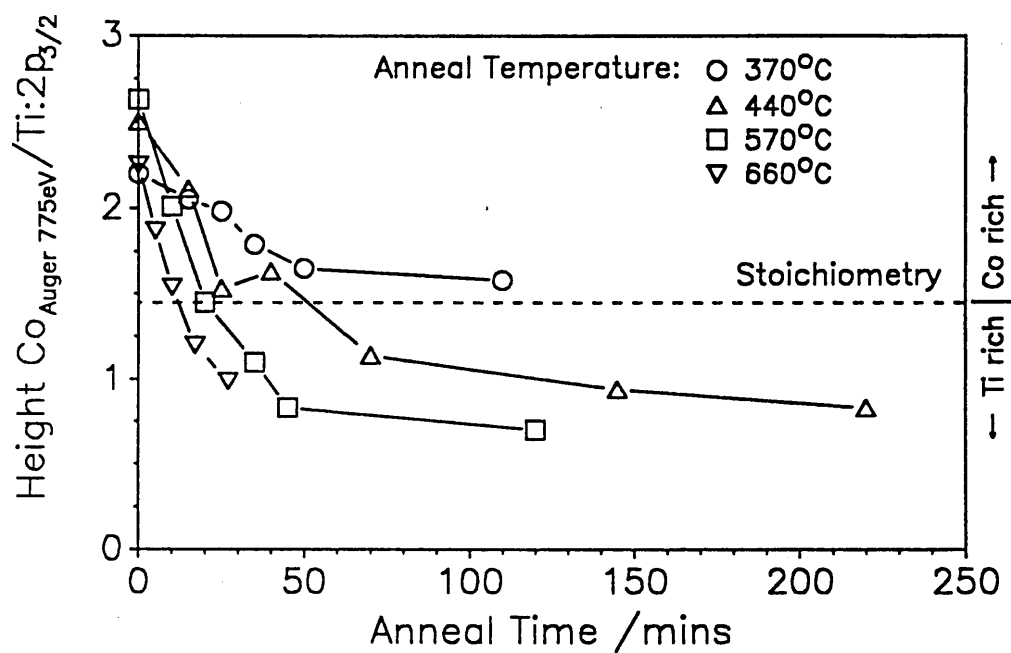


Figure 5.10: The effect of heating on surface segregation of Ti in CoTi. Segregation occurs most efficiently at the highest temperatures to produce a Ti enriched surface. Spectra were measured in the Leybold-Heraeus system and were taken at room temperature.

was observed for all annealing temperatures, but Ti segregation was most pronounced at the highest temperatures.

In the same way, the O:1s/Ti:2p_{3/2} peak height ratio, as shown in figure 5.11, indicates an increased surface oxygen concentration with annealing. Heating at 370 or 440°C produces a slight increase in the O:Ti ratio suggesting that, as Ti atoms segregate to the surface, associated O atoms also segregate. However, during the highest temperature anneal (660°C), more pronounced oxygen segregation behaviour is seen, implying that O atoms from within the alloy bulk segregate faster than the Ti atoms. Calibration is achieved more simply in this case from O:1s and Ti:2p sensitivity factors. An O:1s/Ti:2p_{3/2} height ratio of 0.6 corresponds to 1:1 Ti:O surface stoichiometry.

5.5.1 Surface Segregation

Many theoretical treatments have been proposed to predict the equilibrium surface composition of an alloy. Segregation trends based on chemical and elastic (size) effects^{5.27} were largely superseded by models based on surface tension, strain energy and the heat of mixing of the alloy components^{5.28, 5.29}. More refined models include contributions from entropy and short range order^{5.30}. Later, segregation schemes based on electronic factors were reported^{5.31}. As a consequence, segregation behaviour is usually reasonably well predicted by theory, often by a simple model, but several areas of failure have been identified^{5.32}.

In a simple scheme, the driving force toward surface segregation in a *random* binary material is determined by the relative surface energies and the difference in atomic sizes of the components. In a dilute material, strain energy introduced by a large size difference between solvent and solute atoms favours segregation of the solute component^{5.27}. If the difference in atomic sizes is small, then segregation is determined by the minimisation of surface free energy^{5.33}. The surface energy U_0 of an element is a reflection of surface chemical bond strength and is often approximated to the enthalpy of atomisation ΔH_{at} or the surface tension γ of an element. The component with the lowest surface energy shows a tendency to segregate.

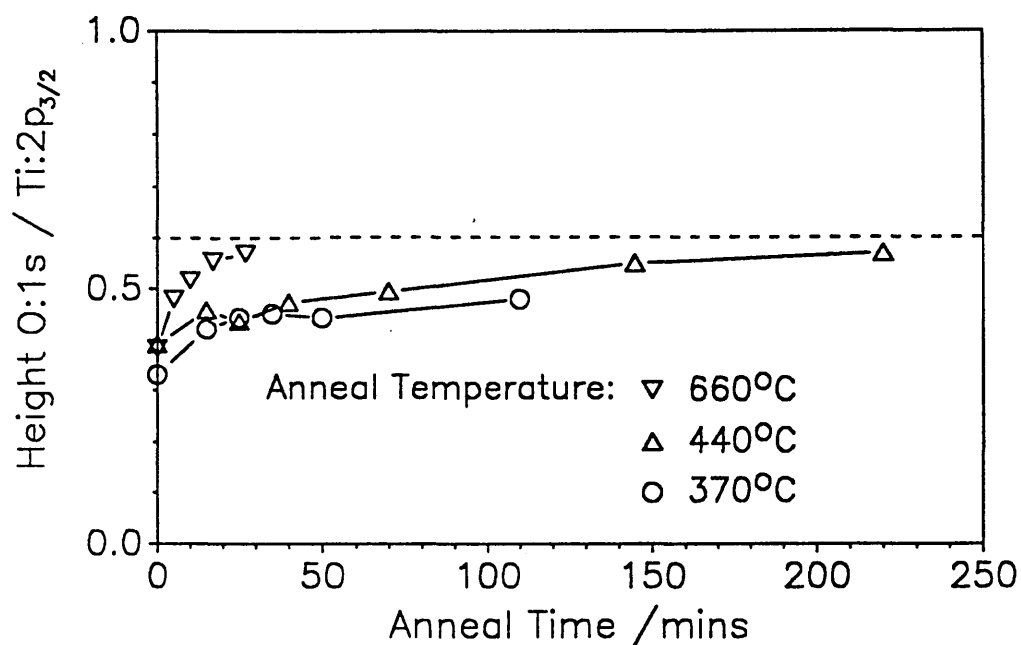


Figure 5.11: Effect of annealing on the segregation of O in CoTi. Segregation of O occurs simultaneously with Ti segregation but is greatest at higher temperatures. The horizontal dashed line corresponds to approximately equivalent Ti and O surface concentrations.

The main opponent of segregation is phase stability^{5.34}. The balance between phase stability and surface energy determines whether segregation of one component will occur.

It is therefore important to consider the effects of various Co-Ti phases which may form when the surface stoichiometry is changed, either by sputtering or annealing. Examination of the bulk phase diagram (shown previously in figure 1.2) demonstrates that a variety of phases may be formed when the alloy surface composition is altered. CoTi in particular has a narrow maximum composition range of only 5.5% (49.7-55.2% Co)^{5.35}. On the Co-rich side of CoTi are two distinct Laves phases; the 'C15' phase (65.5-66% Co) having a cubic structure and the 'C36' phase (68.75-69% Co) having a hexagonal structure. At higher Co concentrations (≈ 75 -80% Co), the compound TiCo_3 may be formed having a f.c.c. (Au_3Cu) structure. No separate phases are reported on the Ti-rich side of CoTi until the ordered compound Ti_2Co . No phase diagram for the Ti-Co-O system has been found. In this work, the stability of Co-Ti-O phases will be very influential as a result of the residual O content at the surface and diffusion of O with Ti observed during annealing.

Ti has a lower surface tension than either Fe or Co ($\gamma_{\text{Ti}}=1.69\text{Jm}^{-2}$, $\gamma_{\text{Co}}=2.25\text{Jm}^{-2}$, $\gamma_{\text{Fe}}=2.08\text{Jm}^{-2}$)^{5.36}, and so is expected to segregate in both FeTi and CoTi if phase stability is overcome. Indeed, pronounced Ti surface segregation has been experimentally observed in single phase FeTi^{5.37}. Surface segregation of Fe has been observed at temperatures above 300°C in FeCo^{5.38} where the differences in surface tension are very much less than for CoTi. The observation of Ti segregation in CoTi here is in broad agreement with surface tension arguments. Obviously phase stability, which will be discussed further below, does not seem to be dominant at this CoTi surface.

5.6 Theories of Sputtering

The ejection of material from a surface by particle bombardment is a complex process which is not yet fully understood^{5.39}. The impact of a high energy noble gas ion at the surface, as is commonly employed in surface preparation, is highly disruptive and can cause severe changes in surface

topography. The basic theory has recently been reviewed by Kelly^{5.40}. A particularly useful measurement of surface erosion is the sputtering yield Y , defined as

$$Y = \text{target atoms sputtered} / \text{incident ions} \quad (5.1)$$

In addition to removal of material from the first layer by simple collision, the particle may penetrate tens of Å into the material, colliding with subsurface target atoms. These physical 'knock-on' effects, the most important sputtering processes for metallic targets, generate a whole cascade of atomic collision events below the surface as shown diagrammatically in figure 5.12. It is the recoil of these atoms to the surface that largely determines the overall sputtering rate.

Furthermore, the transfer of energy to the target atoms around the ion track can cause localised ionisation, excited states or long lifetime defect sites and can lead to 'chemical' sputtering where an unstable surface species is formed. In single crystal targets, disruption generally occurs to a greater depth below the surface as both the incident ion and scattered atoms are 'channeled' down low index crystal planes, especially at certain incident orientations. Effects such as focussing or shadowing may also be important. The channeling of incident ions appears to reduce the overall number of atoms removed from the surface by recoil sputtering^{5.41}.

Attempts have been made to describe the sputtering process in simple mathematics. The most widely adopted simple model is that of Sigmund^{5.42} which uses classical dynamics to describe the changes in incident ion energy and direction as it moves through a random array of point charges of a certain density. Collisions are modelled by electrostatic nuclear repulsion.

The sputtering yield $Y(E)$ of a single element target at an ion energy E can be reasonably calculated using the ideas developed in detail by Sigmund^{5.43},

$$Y(E) = \Lambda F_D(E, \theta, x=0) \quad (5.2)$$

where Λ is a material dependent parameter, determined by the surface energy

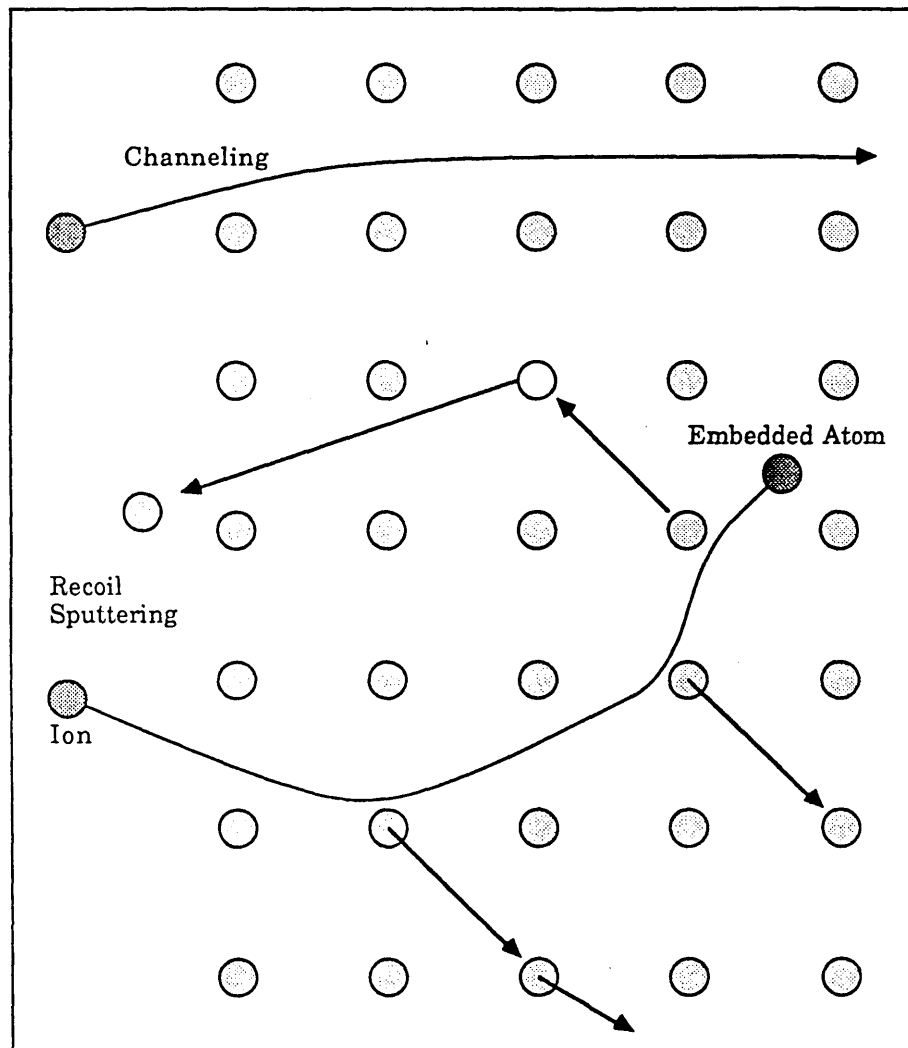


Figure 5.12: Diagrammatic representation of recoil sputtering in single crystal substrates. The incident particle may travel tens of Å into the material, colliding with substrate atoms as it goes and generating 'knock-on' events. The depth of penetration is increased by channelling in single crystal substrates^{5.41}.

of the material (usually approximated to be the heat of atomisation in eV) and the concentration of atoms in the substrate N (in atoms $\text{\AA}^{-3}$) and F_D is characterised by the type, energy E and direction θ of the incident ion. The calculation of $F_D(E, \theta, x)$ represents the depth distribution of the energy deposited by the incident ion. Energy is deposited with depth x as a consequence of collisions between the incident ion and the target atoms as it penetrates into the solid. The target atoms are scattered, producing a 'cascade' of atoms in motion below the surface. Those which recoil back to the surface layer (ie, when $x=0$) with greater energy than required to overcome the potential barrier there, are sputtered.

5.7 Accounting for the Sputtering Behaviour of CoTi

Calculating the sputtering yield $Y(E)$ for Co and Ti metal in the way outlined above gives values of approximately 3.3 and 2.5 respectively for 2keV Ar^+ ions. These figures reflect the weaker bond strength of Co (ΔH_{at})[§]. Similarly, in experiment $Y(2\text{keV } \text{Ar}^+) \approx 2.0$ for Co metal^{5.44, 5.45} and 1.2 for Ti metal^{5.46}. The experimentally and theoretically determined values of $Y(E)$ for Co and Ti are shown in figure 5.13. The experimentally observed Co enrichment of the CoTi surface after Ar^+ sputtering is clearly a reversal of expected behaviour from consideration of the elemental sputtering yields.

5.7.1 Mass Considerations

When atomic masses are similar, chemical bonding is likely to be the determinant of preferential sputtering in binary alloys^{5.47}. Furthermore, Betz^{5.48} has suggested that if the component masses are *very* similar, the component with the lowest surface energy U_0 is preferentially sputtered. Specifically, the atom with the weakest chemical bonding will be lost.

However, CoTi is an ordered single crystal where all bonds are equivalent. Hence, chemical bonding cannot initially be important in this case. The phenomenon of preferential sputtering must therefore reflect

[§] It will be recalled that $\gamma_{\text{Ti}} < \gamma_{\text{Co}}$ although $\Delta H_{\text{at Ti}} > \Delta H_{\text{at Co}}$ because of the larger radius of the Ti atom. The ratio $\gamma_{\text{Ti}}/\gamma_{\text{Co}}$ is roughly $(\Delta H_{\text{at Ti}}/r_{\text{Ti}}^2) / (\Delta H_{\text{at Co}}/r_{\text{Co}}^2)$. The density of Co is almost twice that of Ti.

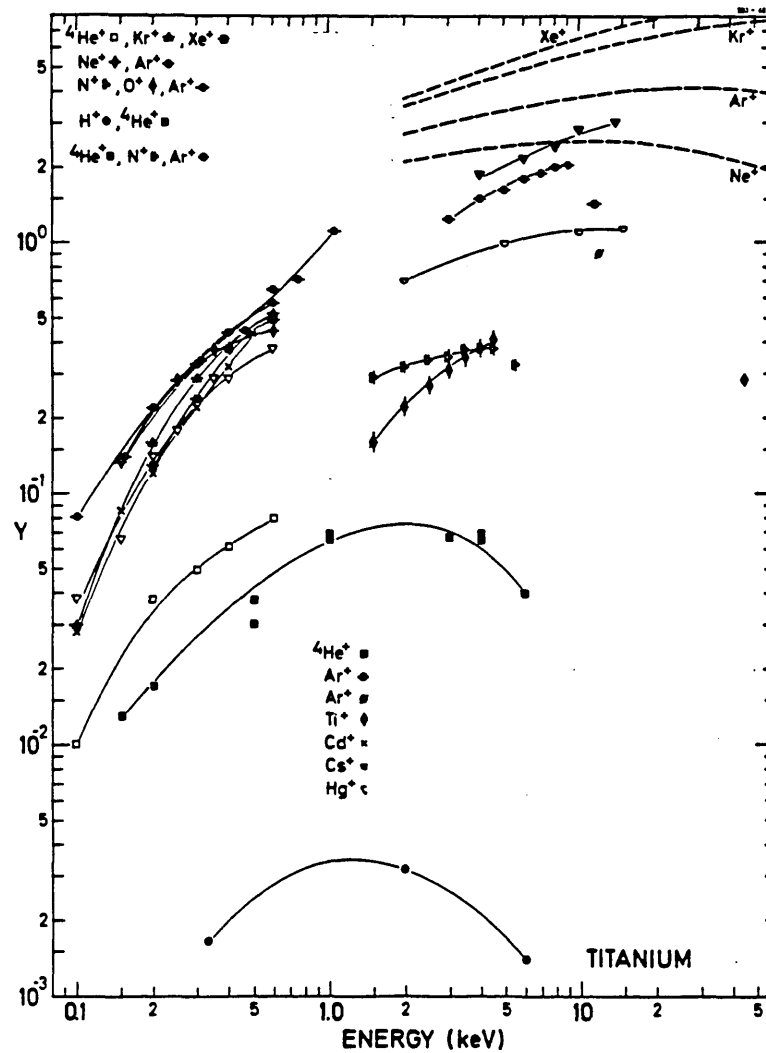


Figure 5.13: Variation of the sputtering yield Y of Ti with ion energy and type^{5.1}. Individual experimental measurements are shown as symbols connected by solid lines. The theoretically calculated sputtering yield is shown for different incident ions as a dashed line.

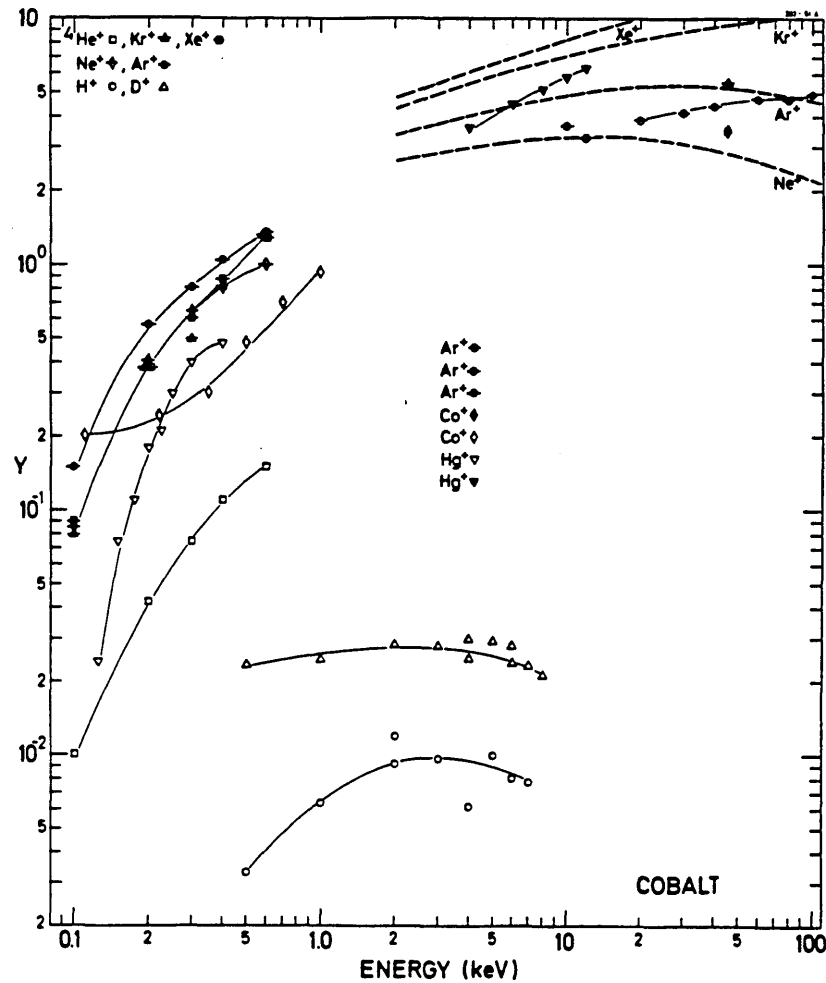


Figure 5.13 (continued): Variation of the sputtering yield Y of Co with ion energy and type^{5.1}. Individual experimental measurements are shown as symbols connected by solid lines. The theoretically calculated sputtering yield is shown for different incident ions as a dashed line.

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atomic mass differences between Co and Ti. The maximum amount of energy transferred to an atom M_B during elastic collision with an incident atom M_A is $4M_A M_B / (M_A + M_B)^{5.49}$. Therefore, the lighter atom will be expected to gain more energy upon collision.

In a model developed by Haff^{5.50}, it was suggested that in the linear cascade regime, many more target atoms are in motion relative to the number of incident ions. If each has approximately the same (small) energy, Haff postulated a diffusion-like motion of the subsurface atoms,

$$\text{Amount lost} \propto (Dt)^{1/2} \propto v^{1/2} \propto M^{-1/4} \quad (5.3)$$

where D is a 'diffusion constant', v is the atom velocity and M it's mass. Now the ratio of the two sputtering yields is simply,

$$Y_A / Y_B = (M_A / M_B)^{1/4} \quad (5.4)$$

Under such a simple scheme, Y_{Co}/Y_{Ti} is 0.94, implying surface enrichment of Co as observed experimentally, although all surface energy considerations and ion energy dependence are completely neglected.

Kelly^{5.40} has extended the diffusion idea. In this model, the composition of the first atomic layer is dominated by mass and/or bonding considerations, the composition of the second layer is determined by the velocity of surface recession and the segregation ratio (forward (segregation) and backward (solution) atomic jumping frequencies between atoms in the top and second layer) under conditions of particle bombardment.

5.7.2 Bonding Considerations

Bombardment creates extensive disruption of the crystalline structure of CoTi(110), effectively destroying at least some lattice ordering within the ion penetration depth (measured as 20-25Å for 2keV Ar⁺→CuNi^{5.51}) within a short period of time. Bombardment results in recoil mixing and the creation of a large network of vacancies in the near surface region giving rise to enhanced atomic diffusion. This disruption may lead to areas with localised Ti-Ti and Co-Co bonding and hence increase the tendency of Ti to segregate

to the surface due to surface tension considerations. As a result, a proportion of the Co enrichment observed during ion bombardment will be the result of preferential sputtering of these segregated Ti atoms.

5.8 Comparisons with FeTi

It has already been mentioned that there is pronounced Ti segregation in CoTi at temperatures $\geq 370^\circ\text{C}$. In a well ordered CoTi single crystal, intrinsic segregation effects are likely to be very slow at room temperature. Indeed, there is evidence in FeTi(100) that once a sharp 1×1 LEED pattern has been obtained, the extensive Ti segregation experienced during crystal preparation is greatly reduced^{5.52}. Surface tension values for Co and Fe are only slightly different and similar segregation is expected on this basis. In a study of FeCo(100) surface, segregation of Fe was observed (as expected from the lower γ) only in the disordered alloy phase ($>300^\circ\text{C}$). Below the order-disorder transition, no segregation was seen, although bombardment at room temperature did imply Fe segregation. Although Ti segregation was observed experimentally in the present work at room temperature, oxidation of the Ti component of the alloy occurred simultaneously. It is therefore difficult to ascertain whether Ti segregation occurs in the absence of oxygen. Later experiments confirmed that it was not possible to obtain good quality LEED patterns from this CoTi(110) surface.

The reversal of elemental sputtering yields and an apparent inability to explain compositional changes induced by Ar^+ bombardment on the basis of elemental sputtering yields has been observed in FeTi, a closely related intermetallic compound to CoTi. Indeed, observations of Ti segregation/preferential sputtering during the preparation of FeTi surfaces are common^{5.52, 5.53, 5.54, 5.55}.

As an example, single phase 0.5keV Ar^+ sputtered FeTi showed enrichment of Fe at the surface^{5.37} due to preferential sputtering of segregated Ti atoms. The magnitude of the enrichment was similar to that found here and was similarly explained by surface tension considerations ($\gamma_{\text{Ti}}=1.69\text{Jm}^{-2}$, $\gamma_{\text{Co}}=2.25\text{Jm}^{-2}$, $\gamma_{\text{Fe}}=2.08\text{Jm}^{-2}$)^{5.36}. However, contrary to the findings on CoTi here, this work on FeTi demonstrated less marked Fe enrichment using higher incident ion energies. It was suggested that

increased ion range and changes in irradiation enhanced diffusion may account for this phenomenon, which is the reverse of usual trends.

5.9 Removal of Contamination from CoTi

The failure to completely remove the two major contaminant species (C and O) from the CoTi surface by sputtering, was disappointing. Obviously, the growth of the single crystal substrate is likely to be the main source of these atoms in the sample bulk. Estimates of the level of dissolved O in the bulk of the sample range between 500 and 1500 ppm, representing a considerable problem in any future cleaning on an atomic scale^{5.56}. The large concentration of dissolved bulk O and C in the alloy, must account for the major irreducible contamination seen at the alloy surface after extensive sputtering. Unfortunately, prolonged annealing at temperatures $>1000\text{K}$ in UHV, which may ultimately lead to diffusion of bulk dissolved oxygen, leads to visible surface recrystallisation, extensive Ti segregation and macroscopic roughening of the CoTi surface. The influence of dissolved oxygen in CoTi has not been assessed, but work has suggested^{5.57} that the presence of an impurity with a high enthalpy of segregation can strongly affect the segregation characteristics of the main segregating component in binary alloys.

5.10 Conclusions

Compositional changes occur at the CoTi surface when sputtered with Ar^+ ions of between 0.5 and 8keV. An observed enrichment of Co and preferential sputtering of Ti at the surface is expected from mass considerations. It is reasonable to assume that the preferential removal of Ti atoms from the CoTi surface seen during sputtering is at least in part due to bombardment assisted Ti segregation via a large defect network. Titanium segregation is observed at elevated temperatures and is expected from surface energy minimisation considerations. Segregation effects are expected to decrease with increasing crystal perfection although there is a general lack of data concerning segregation and sputtering of binary transition metal single crystals. The inability to completely remove C and O contamination from the sample surface is a reflection of high bulk dissolved values together with surface segregation effects.

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6. The Oxidation of CoTi

6.1 Introduction

In this chapter, the oxidation of single crystal CoTi(110) alloy will be examined. The interaction of O₂ with both the annealed and sputtered CoTi surfaces at room temperature was followed by angle resolved XPS measurements in the ESCALAB spectrometer. These results are compared with the XPS spectra of oxidised Ti presented in chapter 4. XPS spectra are also presented for the interaction of O₂ with Co metal and contrasts between Co, Ti and CoTi alloy oxidation are discussed.

HREELS was performed on annealed CoTi surfaces in the Leybold-Heraeus chamber after exposure to O₂. Comparison will be made with HREEL spectra of the oxidation of elemental Ti. Data is presented in sections 6.2 to 6.5 and discussed further in sections 6.6 to 6.12.

6.2 The Oxidation of Annealed CoTi Followed by XPS

The single crystal CoTi(110) alloy surface was Ar⁺ sputtered in the ESCALAB preparation chamber to produce a surface with minimum C and O levels as judged by XPS measurement. The sample was annealed in vacuum at ≈600°C until the Co:Ti ratio corresponded to 1:1. Unfortunately, such treatment of the CoTi(110) surface did lead to macroscopic surface roughening, and an appreciable concentration of O at the surface, so it was not possible to observe well defined LEED patterns. Hence, results should be regarded as being typical of those of a polycrystalline surface.

After annealing, the XPS intensity ratio measured at 90° take-off angle (normal emission) was Co:Ti:O:C of 1.94 : 1 : 0.18 : 0.012 which corresponds to a stoichiometry of Co_{0.91}TiO_{0.45}C_{0.08}. A change in this ratio to Co:Ti:O:C = 1.17 : 1 : 0.23 : 0.01 corresponds to Co_{0.55}TiO_{0.56}C_{0.07} at the extreme surface measured by 15° take-off angle (grazing emission) XPS, indicating some Ti and O segregation or Co depletion at the very outermost layers.

6.2.1 Ti:2p

Figure 6.1 shows the changes that occur in the Ti:2p core level of annealed CoTi with exposure to O₂ at room temperature taken at normal emission. Before O₂ exposure, the Ti:2p_{3/2} peak maximum is located at 455.1eV and the 2p_{1/2} at 461.1eV binding energy. With oxygen exposure up to 7500L, there is a gradual increase in structure both between the two original 2p peaks and to the high binding energy side of the 2p_{1/2}. After 7500L O₂ exposure, a new Ti:2p doublet is visible, shifted by +3.7eV binding energy and is accompanied by a small shift (+0.2eV) in maximum intensity position of the initial 2p_{3/2} peak.

The changes are more obvious when measured using a more surface sensitive grazing emission (take-off angle of 15° relative to the surface plane) as displayed in figure 6.2. In this way, the effective sampling depth is decreased to about a quarter of the value measured at normal emission. The same features can be observed as above, but the growth of structure seen in normal emission between the original 2p peaks is more pronounced. Even after exposure to only 0.75L O₂, as in shown figure 6.2(b), intensity in the 2p_{3/2} peak has been markedly redistributed, resulting in attenuation of maximum intensity, an increase in peak width (FWHM from 2.4 to 2.8eV) and some shift of peak maximum to higher binding energy. After 300L O₂ exposure, there is clearly an increase in structure between the original 2p peaks and when exposed to 7500L O₂, a separate peak located at 458.8eV becomes distinct. In addition, some structure is observed to the high binding energy side of the original 2p_{1/2} peak centered at about 464.7eV. This new doublet is located at +3.7eV higher binding energy with respect to unexposed CoTi.

6.2.2 O:1s and C:1s

Figure 6.3 shows the increase in the O:1s intensity with oxidation measured at normal and grazing emission. The spectrum in part (a) represents the irreducible O associated with the annealed CoTi surface as discussed in chapter 5. This peak is located at 531.2eV binding energy. With oxygen exposure, the peak grows in intensity and shifts slightly downward in binding energy until after 7500L it is positioned at 530.7eV. No

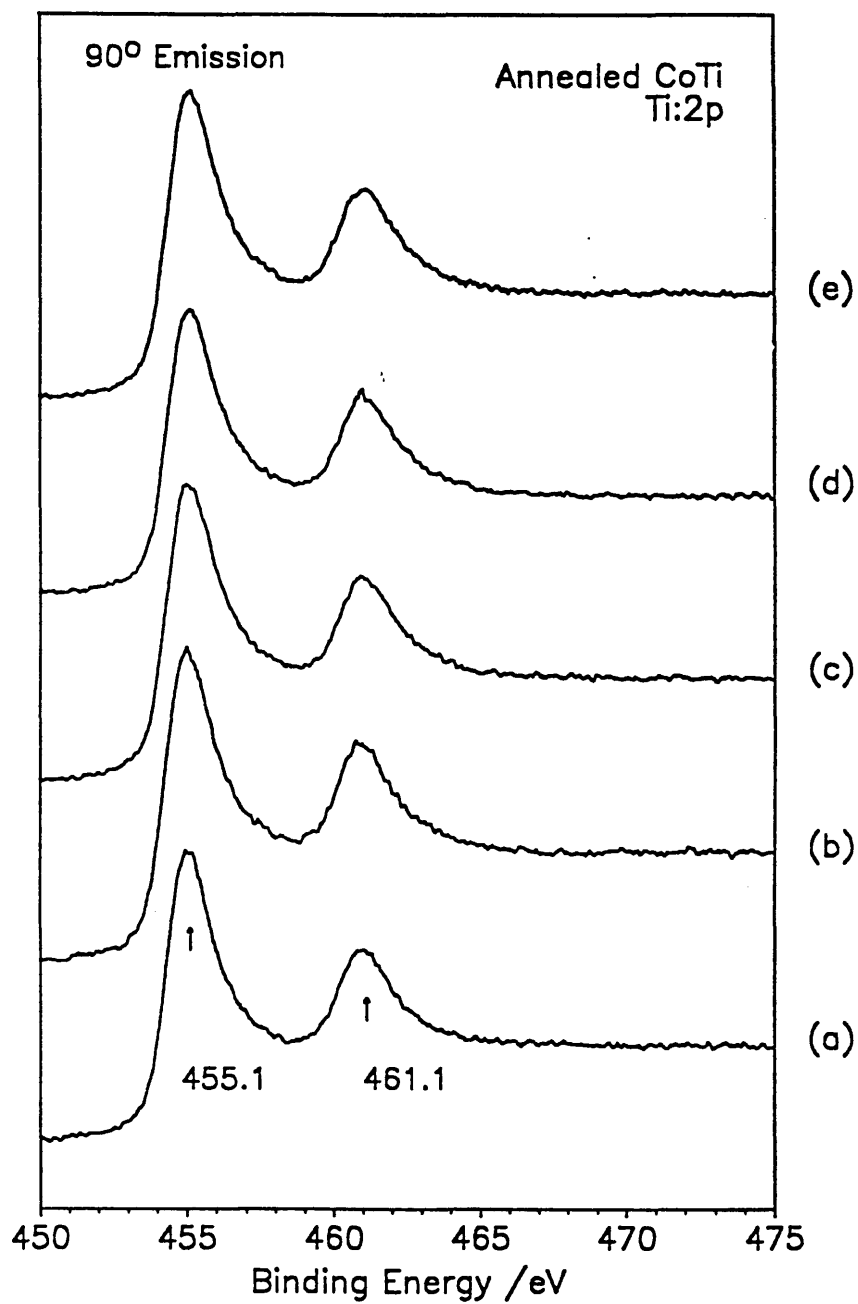


Figure 6.1: Mg $K\alpha_{1,2}$ Ti:2p spectra for CoTi with exposure to O₂ at room temperature measured at normal emission (90° take-off angle) (a) 0L (b) 0.75L (c) 3L (d) 7.5L (e) 30L.

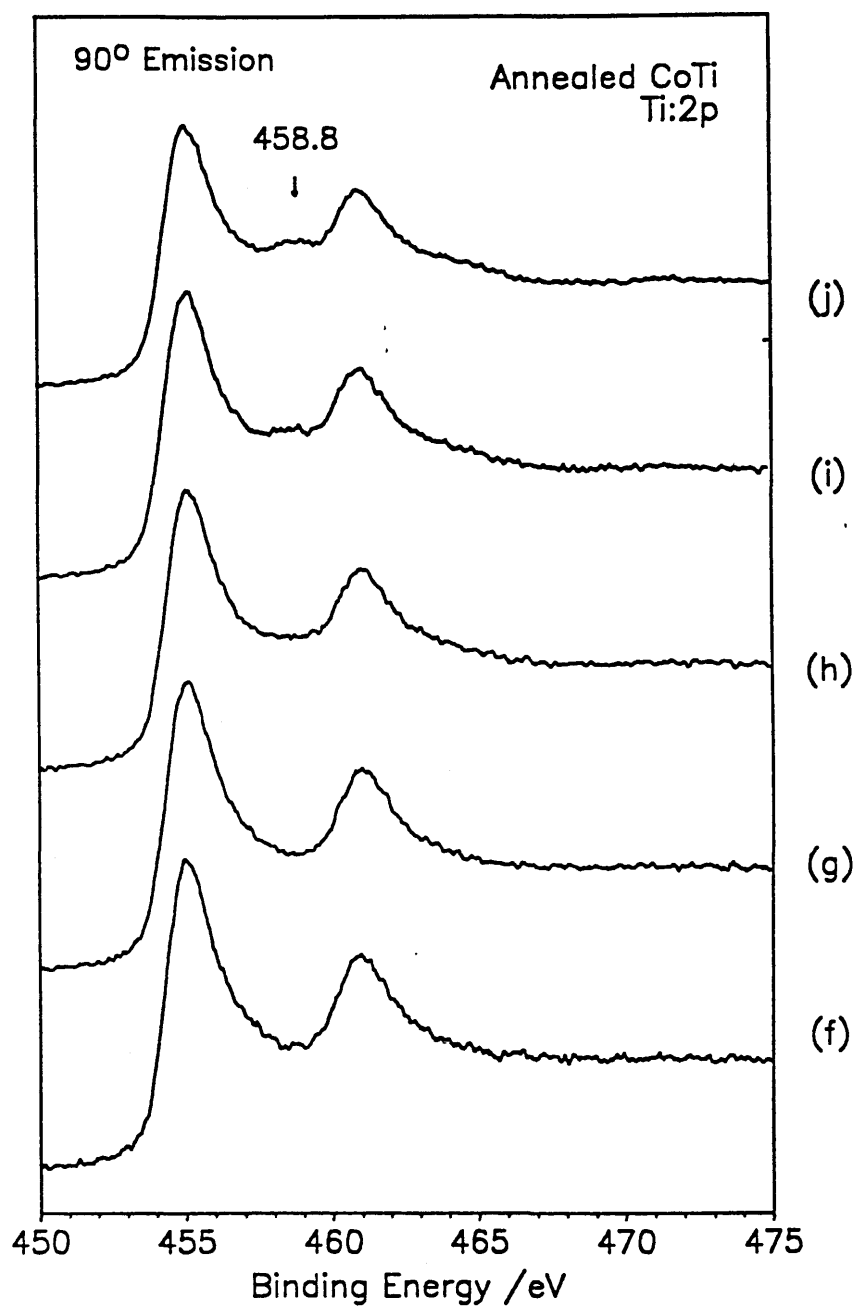


Figure 6.1 (continued): Mg $K\alpha_{1,2}$ Ti:2p spectra for CoTi with exposure to O_2 at room temperature measured at normal emission (90° take-off angle) (f) 75L (g) 300L (h) 750L (i) 3000L (j) 7500L.

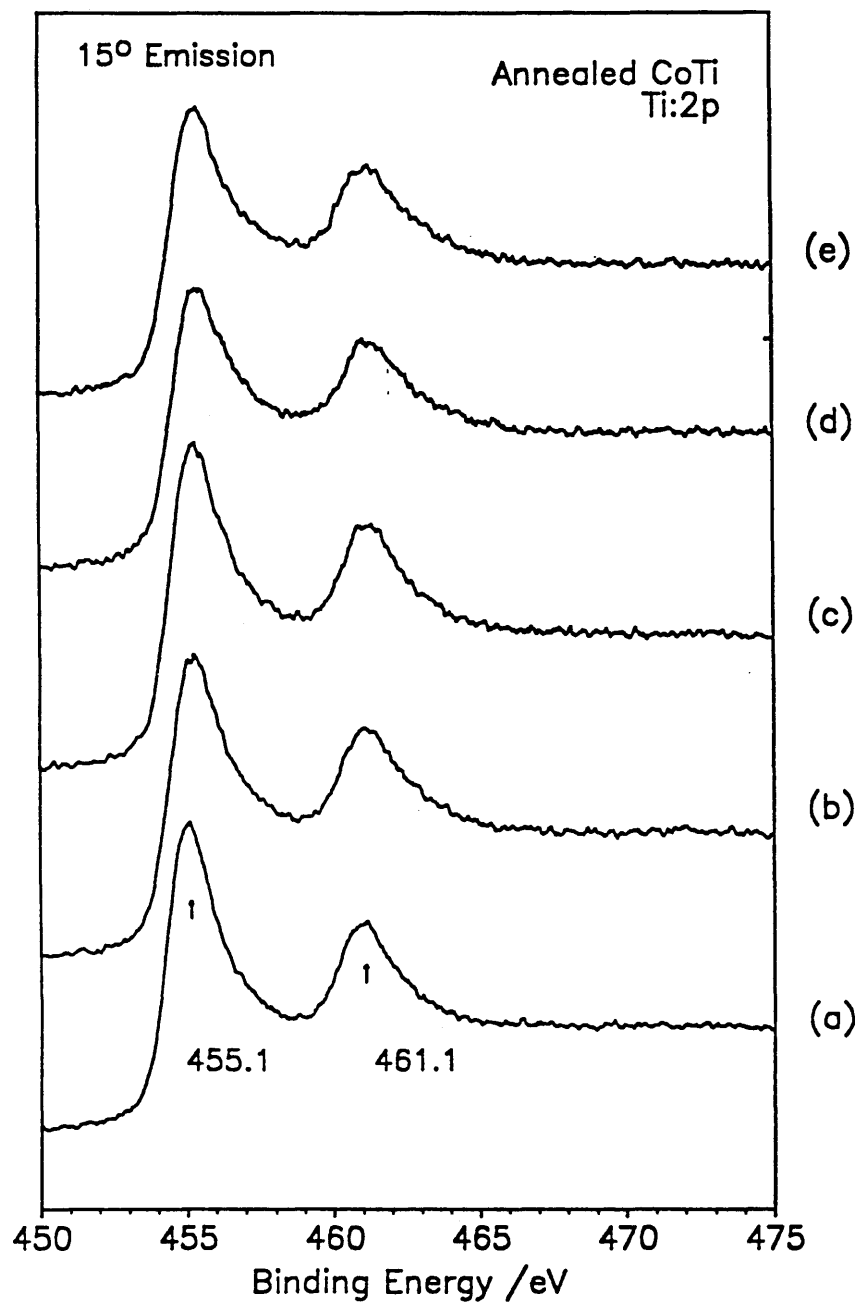


Figure 6.2: Mg $K\alpha_{1,2}$ Ti:2p spectra for CoTi with exposure to O_2 at room temperature measured at grazing emission (15° take-off angle) (a) 0L (b) 0.75L (c) 3L (d) 7.5L (e) 30L.

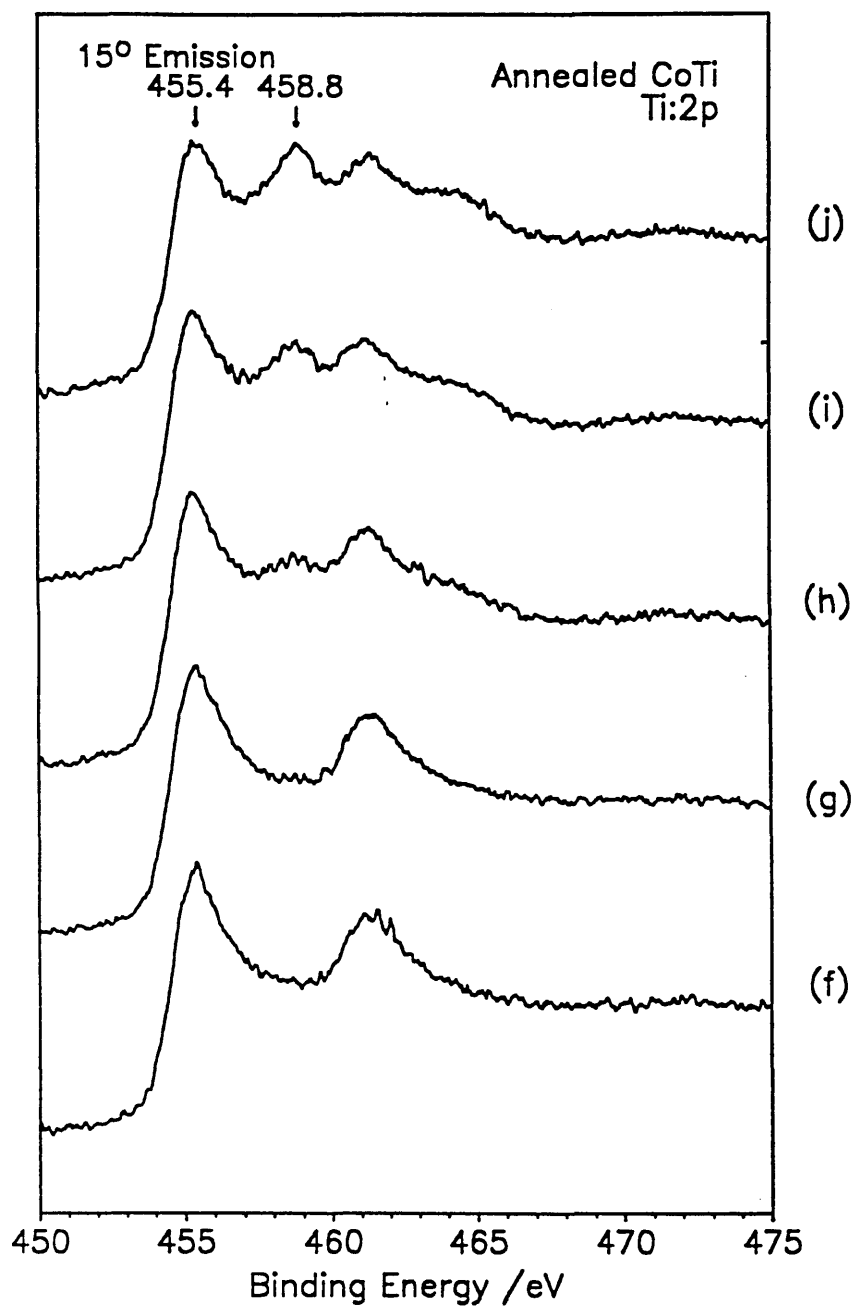


Figure 6.2 (continued): Mg $K\alpha_{1,2}$ Ti:2p spectra for CoTi with exposure to O_2 at room temperature measured at grazing emission (15° take-off angle) (f) 75L (g) 300L (h) 750L (i) 3000L (j) 7500L.

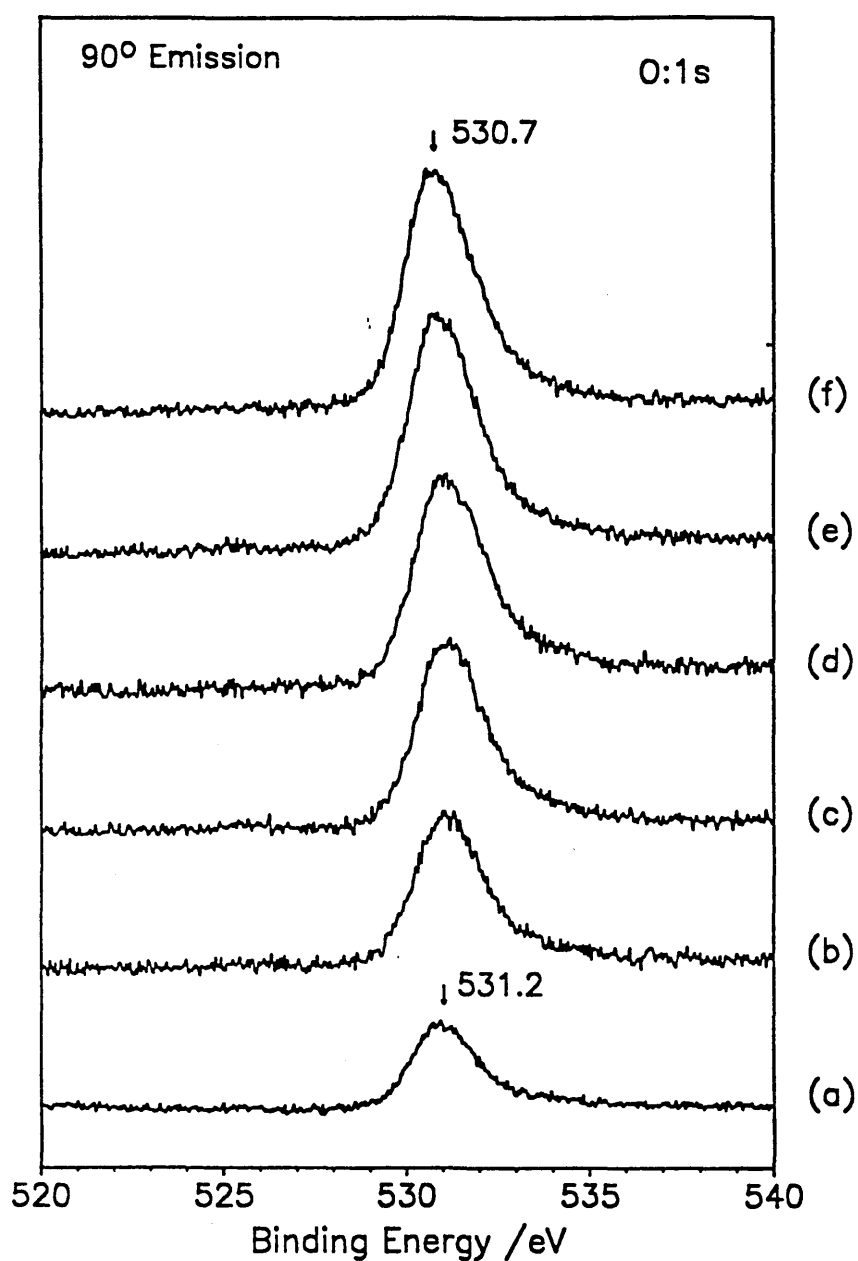


Figure 6.3: Mg $K\alpha_{1,2}$ O:1s spectra for annealed CoTi with exposure to O_2 at room temperature measured at normal emission (90° take-off angle) (a) 0L (b) 0.75L (c) 7.5L (d) 75L (e) 750L (f) 7500L.

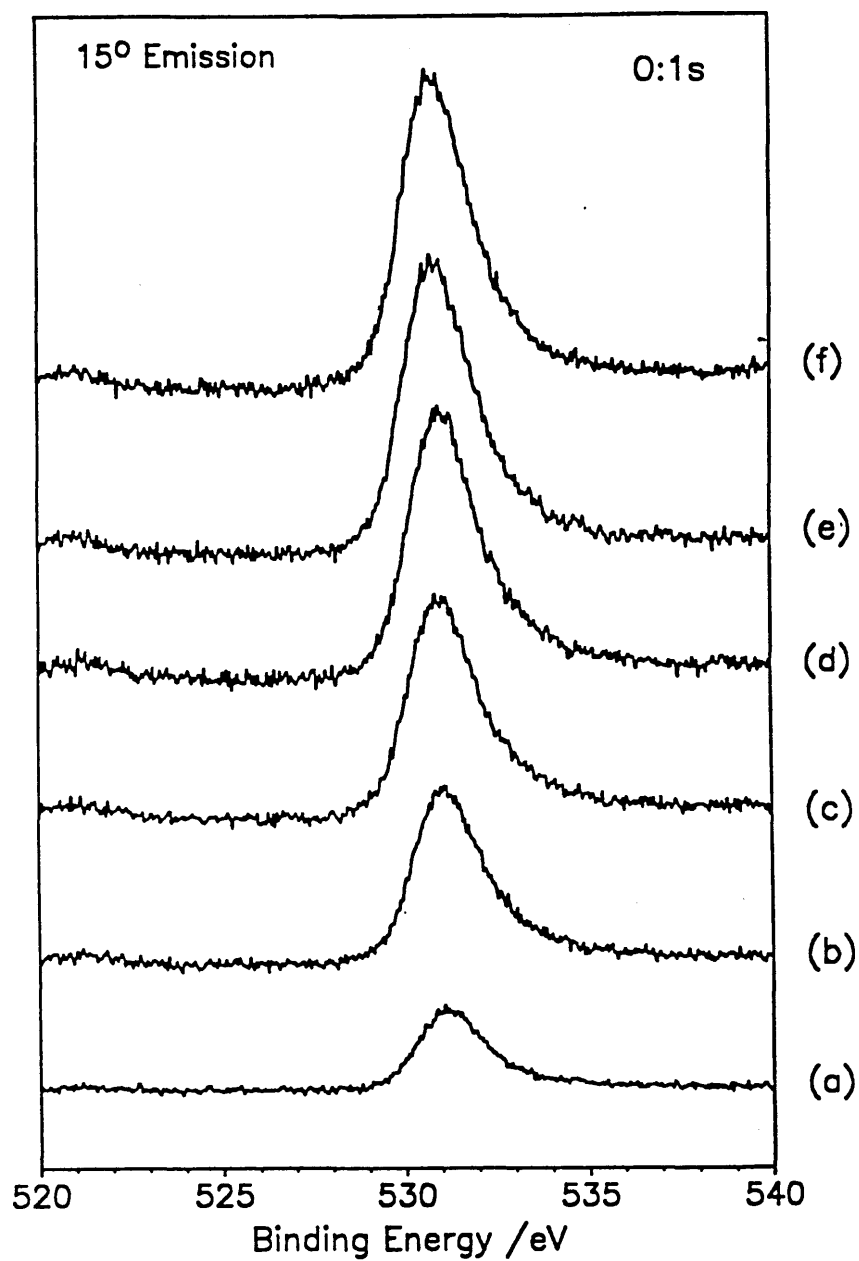


Figure 6.3 (continued): Mg K $\alpha_{1,2}$ O:1s spectra for annealed CoTi with exposure to O₂ at room temperature measured at grazing emission (15° take-off angle) (a) 0L (b) 0.75L (c) 7.5L (d) 75L (e) 750L (f) 7500L.

discernible change in peak shape or width (FWHM=2.0eV) occurs.

Measurement of the C:1s core level region (not shown) shows that some C (<10%) is present in the form of a metal carbide species which cannot be removed by sputtering. The intensity of the C:1s feature decreases during oxidation indicating that C is buried by the oxide layer. Therefore, it is possible to discount interaction of CoTi with residual vacuum CO (or CO₂) to any great degree during oxygen exposure. It has been reported that CO does not dissociate on polycrystalline Ti^{6.1} and that Ti oxides are not formed as a result of exposure to CO^{6.2} although evidence has been produced recently which suggests that adsorption of CO on Ti is dissociative (with low dissociation rates at room temperature) and leads to oxidation to Ti²⁺ species only^{6.3}.

6.2.3 Co:2p

In contrast to the relatively large changes seen in the Ti:2p region, the Co:2p core level region shows no obvious change with O₂ exposure except an attenuation in peak intensity. The Co:2p spectra of CoTi, before and after 7500L O₂ exposure, are shown in figures 6.4(a) and (b) respectively. Figures 6.5(a) and (b) show the same information but measured at grazing emission. Both the initial and 7500L O₂ exposed spectra display identical spin-orbit split 2p regions with the 2p_{3/2} at 778.3eV and the 2p_{1/2} at 793.3eV binding energy. The appropriately scaled difference data are shown in figures 6.4(c) and 6.5(c). Loss in 2p intensity relative to the inelastic background occurs in both cases, but is more pronounced at the smaller emission angle.

6.2.4 Valence Band Spectra

The Mg XPS valence band spectra of annealed CoTi is shown in figure 6.6. It shows a mixed Co-Ti:3d band at E_F with some structure due to O:2p just below this. The O:2s peak occurs at ≈23.5eV but is partially obscured by x-ray satellite structure from the Ti:3p peak. The Ti:3p peak is present as a well-defined doublet with a tail to high binding energy. Spin-orbit splitting for the Ti:3p region is not expected to be resolved at this experimental resolution (see chapter 4) and so the double peak structure must be indicative of chemically shifted species. One peak occurs at 33.2eV and

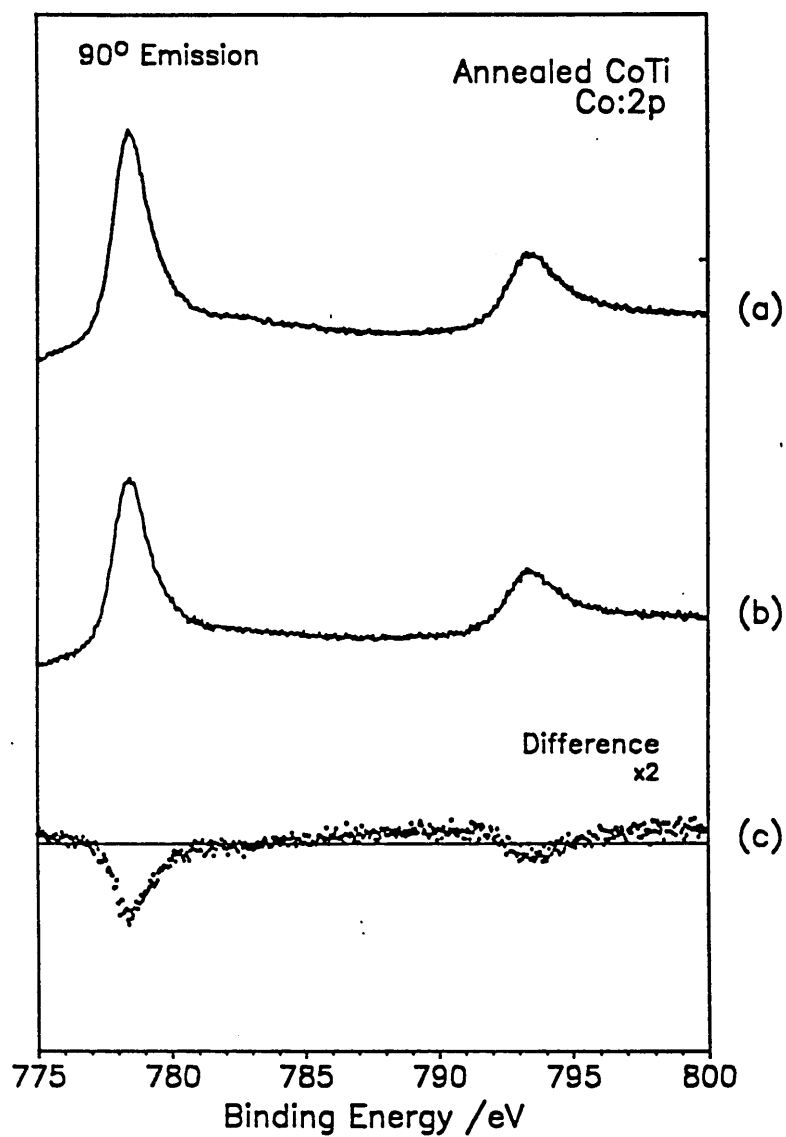


Figure 6.4: Mg $K\alpha_{1,2}$ Co:2p XPS of annealed CoTi measured at normal (90°) emission (a) 0L (b) 7500L O₂ exposed (c) difference (a-b).

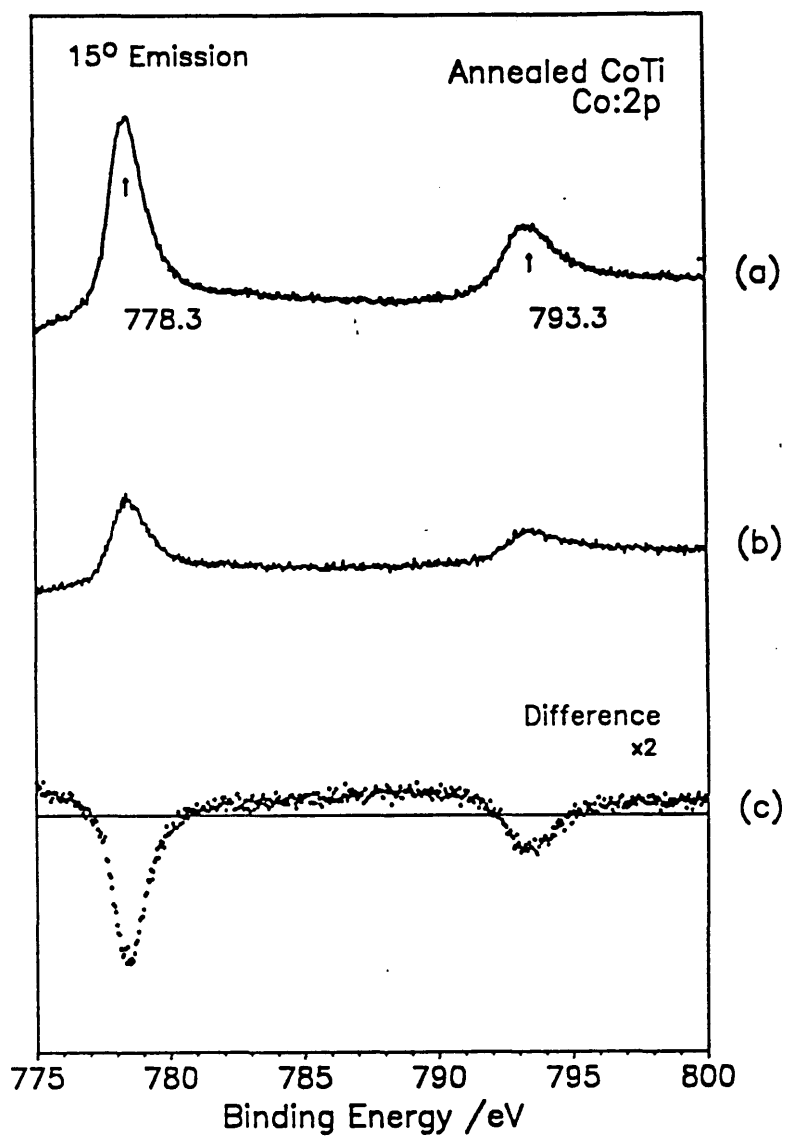


Figure 6.5: Mg $K\alpha_{1,2}$ Co:2p XPS of annealed CoTi measured at grazing (15°) emission (a) 0L (b) 7500L O₂ exposed (c) difference (a-b).

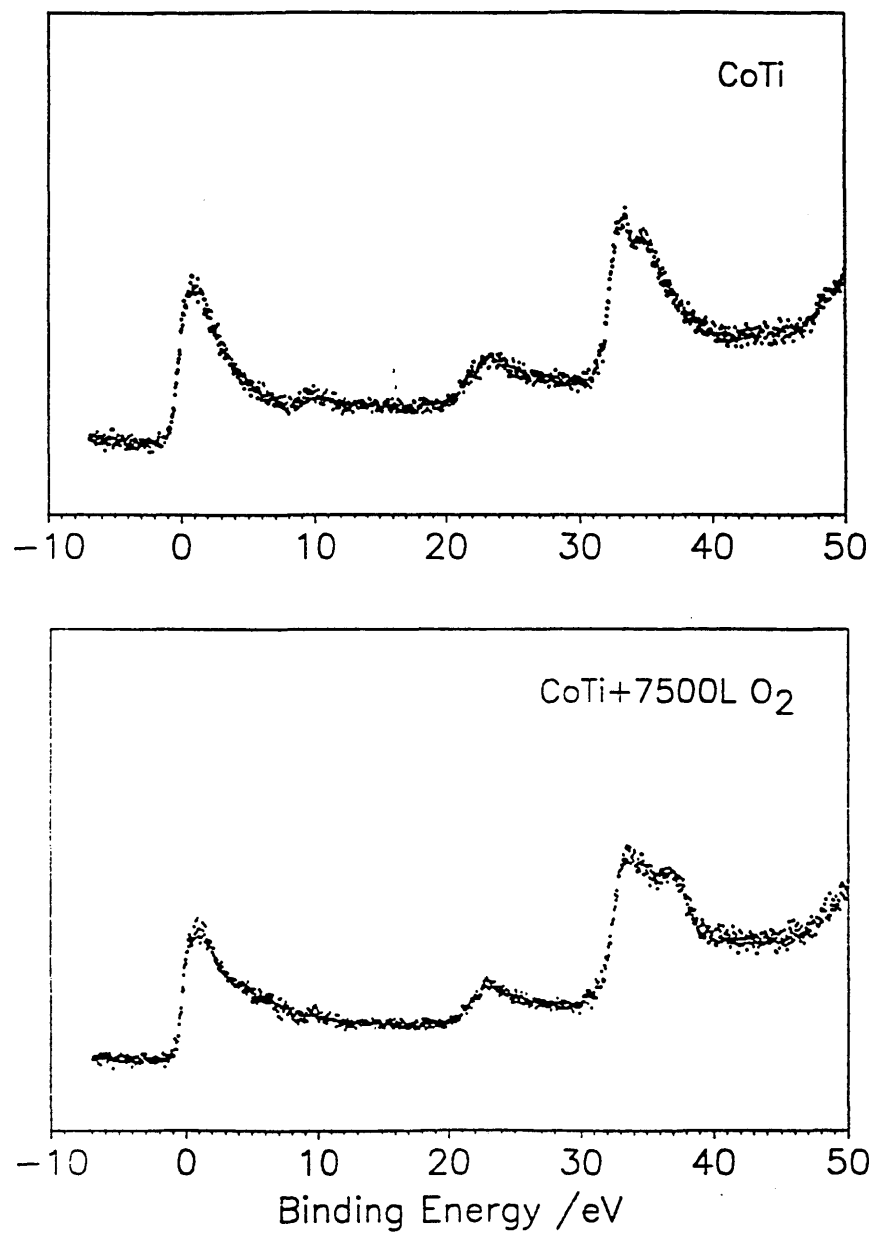


Figure 6.6: Upper panel: Mg ($h\nu=1254\text{eV}$) excited valence band features of annealed CoTi. Lower panel: Valence band of annealed CoTi exposed to 7500L O₂ at room temperature. Note decrease in 3d intensity at E_F and increase in Ti:3p width at $\approx 35\text{eV}$.

the other at 34.8eV. The valence band of CoTi exposed to 7500L O₂ shows an attenuation of d-band intensity at E_F with increased O:2p intensity situated at 3-8eV binding energy. Further changes can be observed in the Ti:3p region, where complex structure is observed. In this region, two broad peaks are situated at 33.3eV and 37.2eV. Once again, changes in the O:2s region at 20-25eV are masked by K α _{3,4} satellites.

6.3 The Oxidation of Sputtered CoTi followed by XPS

The reaction of oxygen with the unannealed CoTi surface was also studied by Mg XPS. The surface was etched by 1.5keV Ar⁺ ions until no change in the Co:Ti ratio occurred with further bombardment (steady state). Although some oxygen contamination of the surface was seen, no C:1s signal was detected. The initial composition of the surface was somewhat Ti-deficient compared to the annealed surface (corrected Co:Ti ratio 1.05:1) which is an artefact of the etching procedure as has already been discussed.

6.3.1 Ti:2p

It can be seen that by comparing the Ti:2p core levels of the sputtered CoTi with the annealed surface (figure 6.7(a) and 6.1(a) respectively), the lineshape of the former is very different. It exhibits a broad 'tail' to high binding energy making the peak appear noticeably asymmetric. In addition, the maximum 2p_{3/2} intensity occurs at a lower binding energy of 454.5eV compared to 455.1eV for the annealed surface. The magnitude of the spin-orbit splitting (BE 2p_{1/2}-2p_{3/2}) is found to be 5.9±0.1eV comparable with that measured on the annealed surface. Some broad structure is observed to the high binding energy side of the 2p_{1/2} peak at around 465eV.

Figure 6.7 shows the changes that occur to the Ti:2p core level spectra of sputtered CoTi upon exposure to O₂ at room temperature as measured by Mg K α XPS at 90° emission. After exposure to 7.5L O₂, both 2p peaks have broadened noticeably and the broad feature at ≈465eV has increased in intensity. By 75L, a new spin-orbit split doublet is visible and after 15000L O₂, the doublet is well resolved and is shifted +4.4eV with respect to the original peaks. This doublet appears at the same energy as that observed upon oxidation of the annealed surface discussed above.

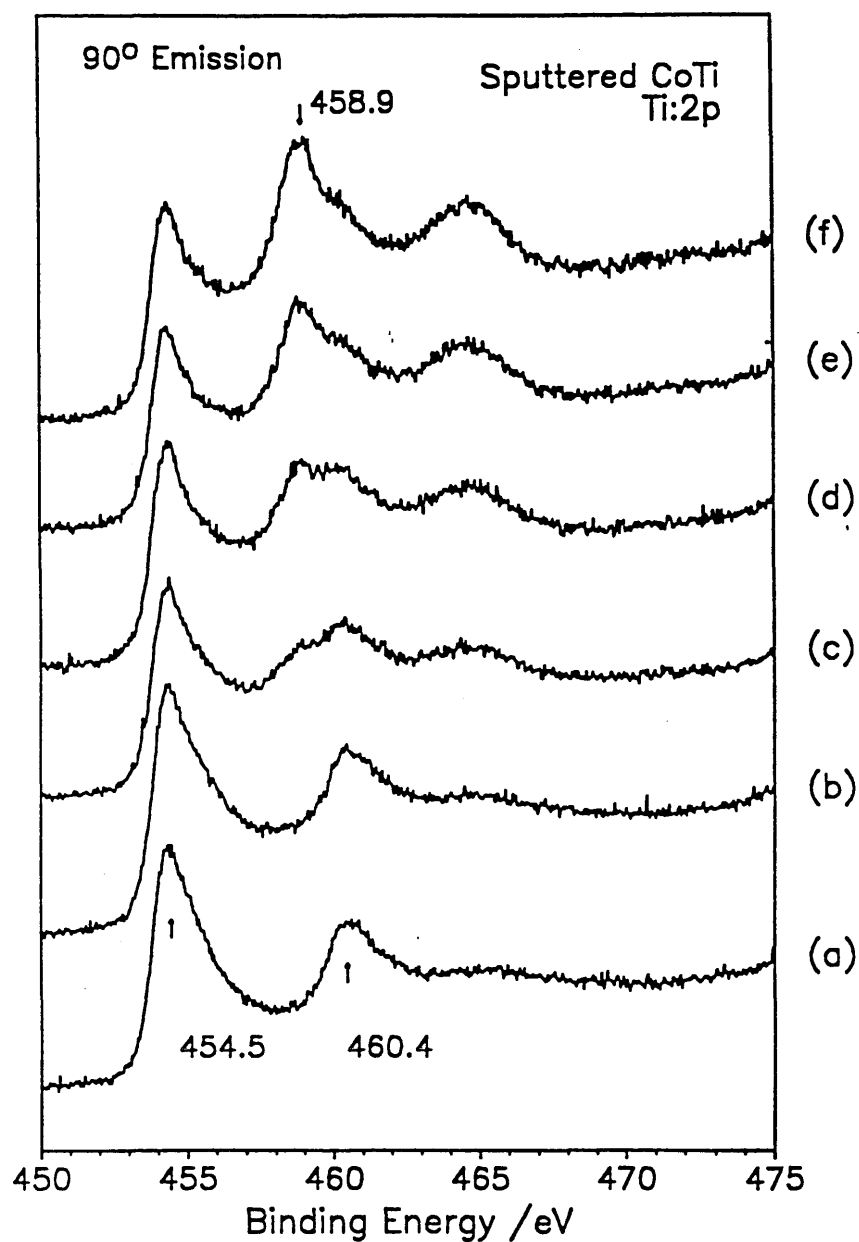


Figure 6.7: Mg $K\alpha_{1,2}$ XPS spectra of Ti:2p region of sputtered CoTi exposed to O_2 at room temperature (a) 0L (b) 7.5L (c) 75L (d) 750L (e) 7500L (f) 15000L. Spectra measured at normal emission.

Comparison with figure 6.1 demonstrates the growth of intensity due to this oxide is much more pronounced on the sputtered surface.

6.3.2 Co:2p and O:1s

The growth of intensity in the O:1s region of the unannealed CoTi surface (not shown) parallels the behaviour of the annealed surface. The initial peak is located at $\approx 531.1\text{eV}$ binding energy, is reasonably symmetric and does not change shape noticeable with O_2 exposure. It shifts downward to 530.6eV binding energy after 15000L O_2 .

Again, the Co:2p spectra of the sputtered alloy surface remain unchanged up to 15000L O_2 exposure. Some attenuation of peak intensity is observed as displayed in figure 6.8 but otherwise, little change occurs. The peak maximum of the Co:2p_{3/2} peak is at 778.4eV and the magnitude of the spin-orbit coupling (15.0eV) is identical to the annealed surface.

6.4 The Oxidation of Co Metal

The discovery that there is no chemical shift in the Co:2p core level spectra of CoTi alloy with exposure to moderate doses of oxygen is rather surprising. To confirm that no oxidation of Co occurs, and that it indeed remains as Co (0), the XPS spectrum of both clean and oxidised Co metal surface was measured to establish the changes accompanying oxidation.

The 2p core level Mg XPS of clean Co foil is shown in figure 6.9(a). The Co:2p_{3/2} and 2p_{1/2} are at 778.2eV and 793.2eV binding energy respectively. The oxidation of Co foil is signalled by the emergence of intensity shifted to higher binding energy, as shown in figure 6.9(b). After 7500L O_2 , new features are clearly visible shifted by $+2.0\text{eV}$ binding energy, together with features shifted $+8.0\text{eV}$ binding energy with respect to the metal 2p_{3/2} and $+9.3\text{eV}$ with respect to the 2p_{1/2}. The O:1s region also shown in the figure displays the growth of two superimposed features at 529.6eV (more intense) and 531eV (less intense). The measured XPS intensity ratio O:Co of 0.12 indicated a surface oxide of $\text{CoO}_{0.62}$ stoichiometry formed after exposure to 7500L O_2 at 300K .

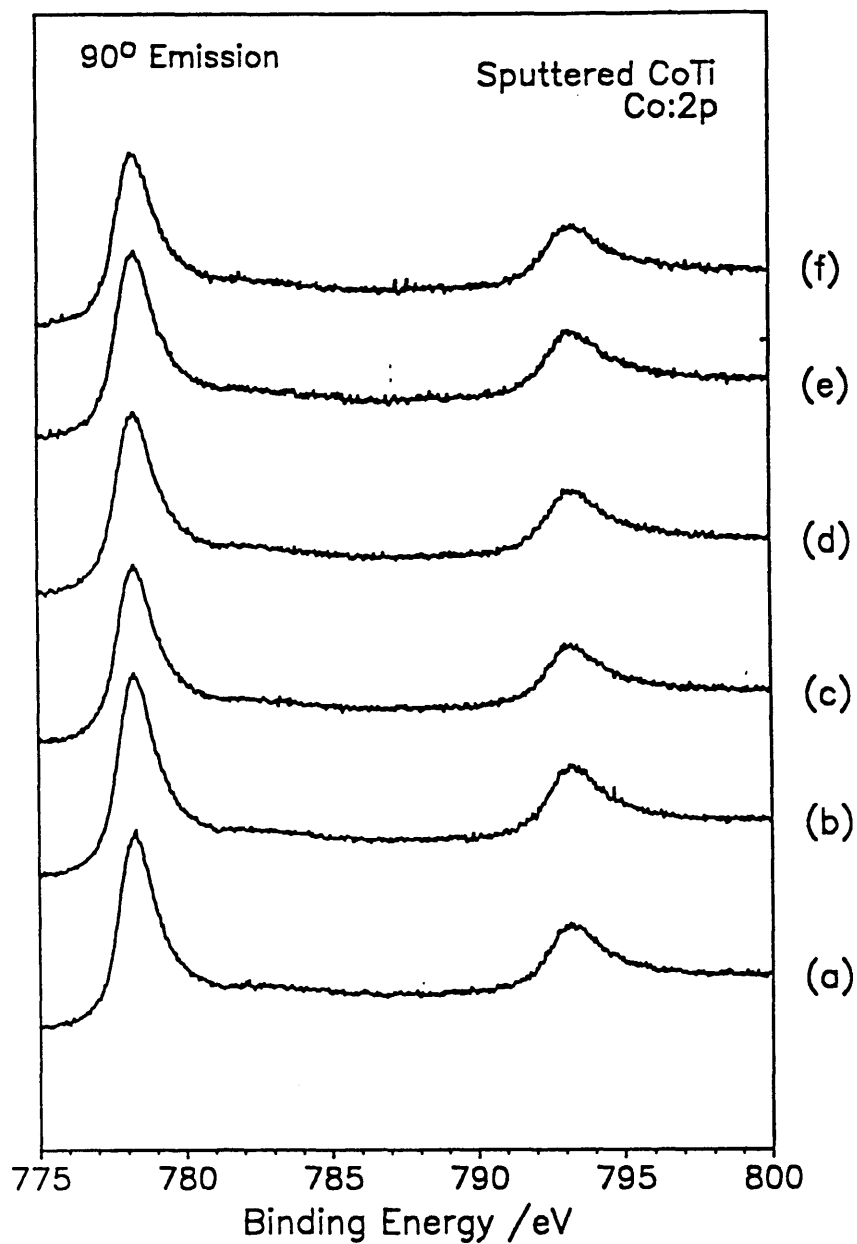


Figure 6.8: Mg $K\alpha_{1,2}$ XPS spectra of Co:2p region of sputtered CoTi exposed to O_2 at room temperature (a) 0L (b) 7.5L (c) 75L (d) 750L (e) 7500L (f) 15000L. Spectra measured at normal emission.

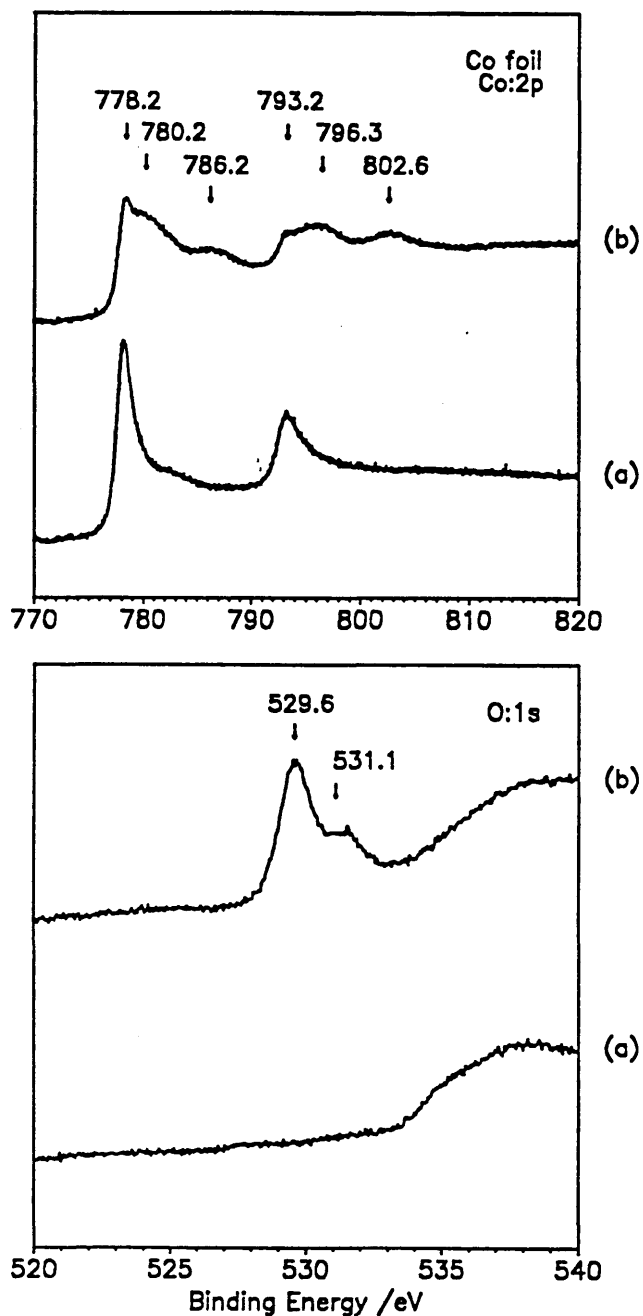


Figure 6.9: Upper panel: Mg $K\alpha_{1,2}$ XPS of (a) Co:2p region of clean Co foil (b) and exposed to 7500L O₂ at room temperature showing the appearance of chemically shifted and satellite features. Lower panel: (a) the O:1s region of clean Co foil and (b) after exposure to 7500L O₂. The higher energy peak is due to contamination and is not intrinsic to CoO.

The appropriately scaled Co:2p difference data of Co exposed to 7500L O₂ and clean Co metal, is shown in figure 6.10. Loss in 2p_{3/2} intensity is maximum at 778.2eV, corresponding to the binding energy of elemental Co. Intensity growth is maximum around 780.4eV and 786.3eV, shifted +2.2 and +8.1eV with respect to the original 2p_{3/2} peak. Changes in the 2p_{1/2} region are qualitatively similar, but intensity growth is shifted by +3.1 and +9.4eV binding energy.

The valence region of Mg K α excited XPS of clean Co, displayed in figure 6.11, shows a narrow Co:3d band at E_F. The spectrum of Co exposed to 7500L O₂ shows an attenuation and broadening of the d band region together with the appearance of some weak O:2s structure at $\approx$ 22eV.

6.5 HREELS of the Interaction of Annealed CoTi with O₂

A typical HREEL spectrum of the annealed CoTi(110) surface measured with a beam energy of 5eV is shown in figure 6.12(a). It shows a single broad loss feature at 65meV. There is unresolved intensity both between the elastic peak and this feature, and as a tail to the high energy loss side of the feature. There are no other peaks located at higher loss energy.

The evolution of the HREEL spectra with oxygen exposure of the CoTi surface are also shown in figure 6.12. The growth of a feature at $\approx$ 90meV is observed, and after 4000L O₂ at room temperature, is as intense as the 65meV feature. Figure 6.13 plots the growth of the loss intensity for the annealed CoTi surface and for Ti(0001) and demonstrates a less rapid uptake of O, together with considerable initial loss intensity on the CoTi surface. However, there is no clear emergence of a single dominant loss peak at 90-95meV as was observed in the case of Ti(0001), and spectra remain disappointingly ill-structured.

6.6 Discussion

6.6.1 Previous Studies of Co Oxidation

The oxidation of Co metal and the identification of Co oxides has been investigated by AES and XPS by several authors^{6.4, 6.5, 6.6, 6.7}, and

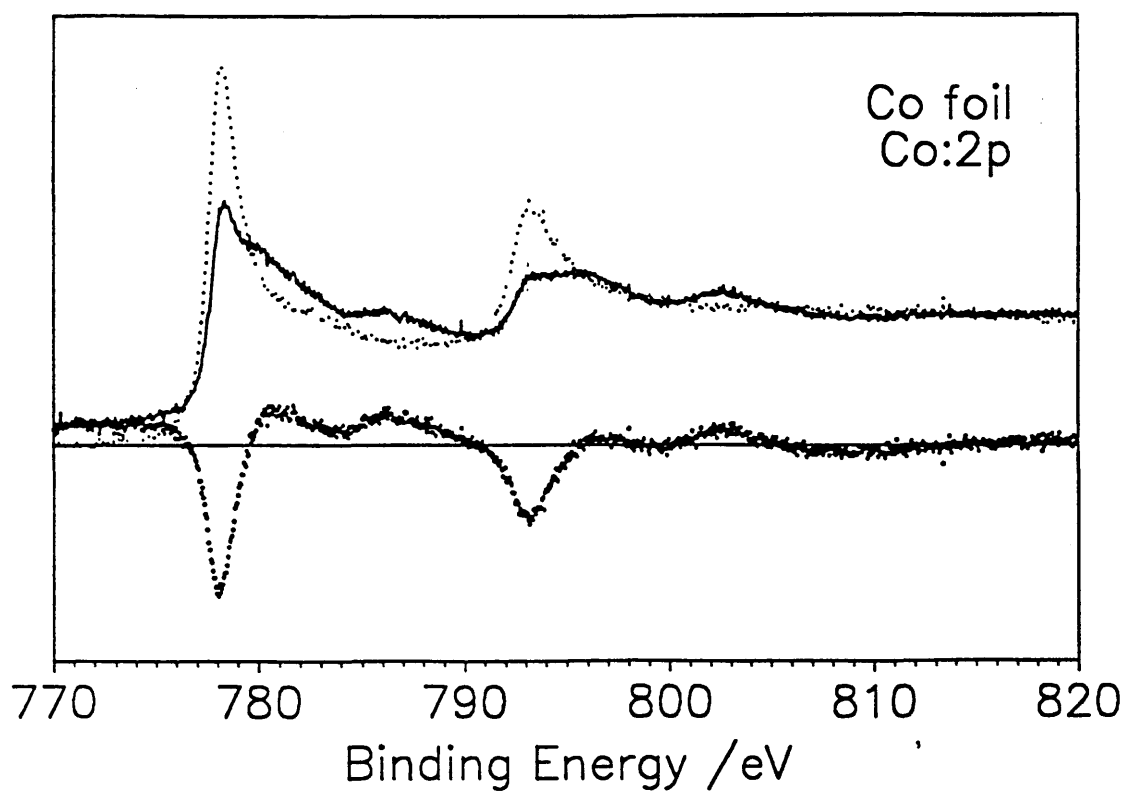


Figure 6.10: Co:2p region of Co foil from figure 6.9. The light dots represent the Co:2p Mg XPS spectrum of clean Co foil, the solid line is the scaled spectrum after exposure to 7500L O₂ and the heavy dots are the difference data (clean minus oxidised). Maximum intensity loss corresponds with the binding energy of Co (0) at 778.2eV binding energy.

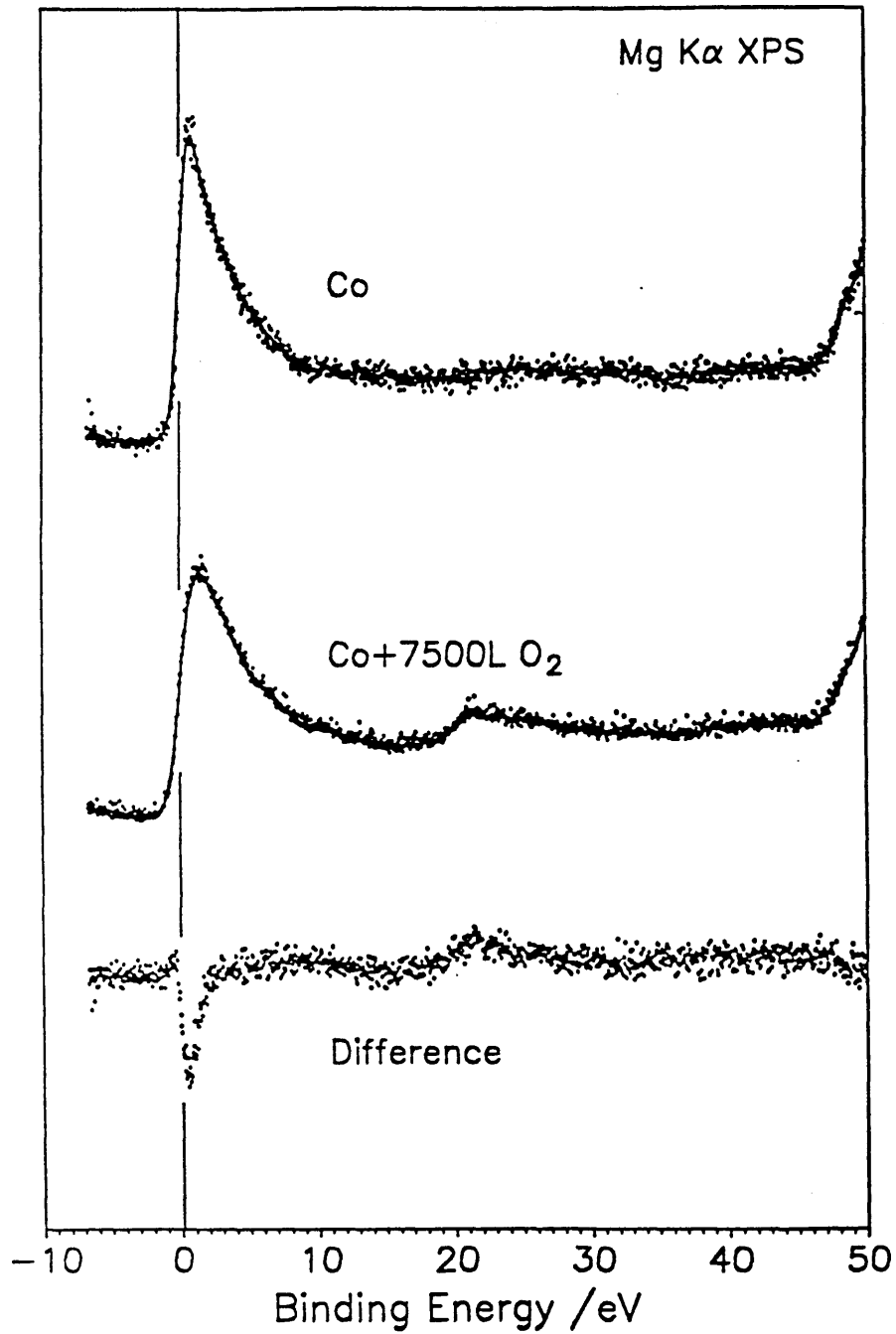


Figure 6.11: Mg K $\alpha_{1,2}$ valence band of (upper) clean Co foil (middle) Co foil exposed to 7500L O₂ at room temperature (bottom) difference data showing decrease in 3d structure at E_F and increase in O:2s features at ≈ 22 eV.

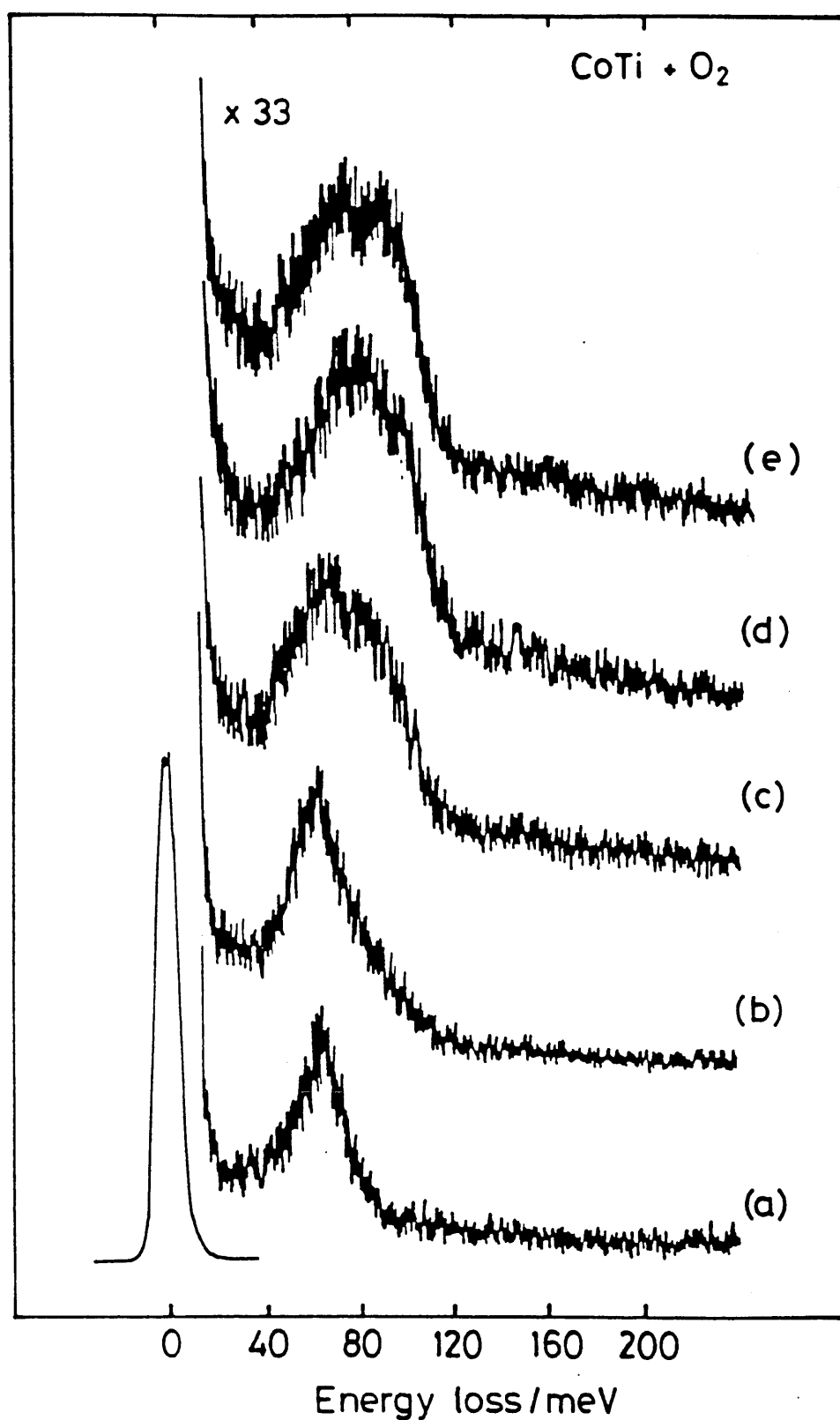


Figure 6.12: HREEL spectra ($E_p=5\text{eV}$) of annealed CoTi surface exposed to O₂ at room temperature (a) 0L (b) 1L (c) 2.2L (d) 7L (e) 4000L. $\theta_i=\theta_s=60^\circ$.

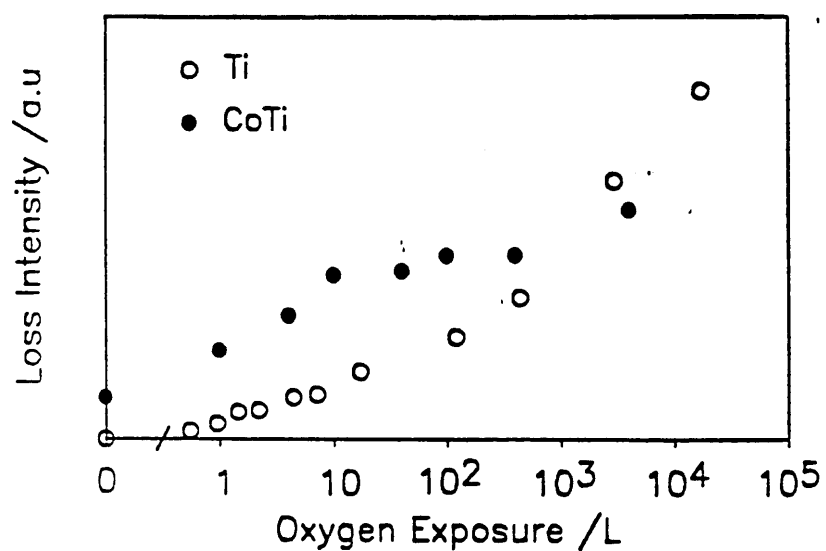


Figure 6.13: Integrated loss intensity (arbitrary units) of features seen in HREEL spectra of CoTi and Ti(0001) relative to elastic peak intensity. Note the less rapid rise in loss intensity on CoTi and the irreducible intensity associated with O at the annealed surface.

again the oxidation products have been variously identified as CoO^{6.8, 6.9, 6.10, 6.11, 6.12}, Co₂O₃^{6.13} and Co₃O₄^{6.14, 6.15, 6.16}.

A detailed XPS study was undertaken on an evaporated Co film by Brundle *et al*^{6.11, 6.12}. Comparison of XPS lineshapes from oxygen exposed polycrystalline Co foil with reference Co compounds, including CoO, Co₃O₄, Co(OH)₂ and CoO(OH), led to the conclusion that the surface oxide formed after $\approx 10^4$ L O₂ exposure is predominantly CoO. The oxide formed after exposure to air (the presence of water) is a mixture of CoO and Co₃O₄ together with cobalt hydroxides, CoOOH and Co(OH)₂. This may account for the variety of compounds proposed by other authors as oxidation products.

Oxygen exposure is accompanied by changes in the Co:2p region; a broadening and shift of the Co:2p peaks and the growth of satellite structure very similar to that observed here. The various Co:2p_{3/2} peak binding energies (BE), core level chemical shift (Δ) and satellite lines observed here are compared with those of published data in table 6.1. Also shown are the corresponding oxidation state (OS) and coordination geometry (Coord) of each of the representative compounds. By examining the data, it is possible to assign the oxidation product observed here on polycrystalline Co as CoO.

It is tempting to assign the double O:1s intensity seen in figure 6.9(c&d) to the two Co-O configurations seen in Co₃O₄ but correlation of the two peak area ratios with exposure suggests that the 531.1eV peak is not associated with O₂ exposure at all, but increases with time in the spectrometer. It was suggested by Brundle *et al* that the feature is due to chemisorbed CO from the vacuum, but it is possible that it could also be due to -OH (O:1s located at 531.2eV in both CoOOH and Co(OH)₂^{6.4}).

6.6.2 The Chemical Shifts of Co Oxides

It is worth digressing momentarily to explain the satellite structure and chemical shifts associated with the oxides of the latter first-row transition metals (Fe, Co, Ni, Cu). The differences seen in the shake-up structure and core level shifts of the various Co oxides can be understood by considering their electronic and structure and geometry. Satellite features in these compounds are largely the result of final state configuration interactions.

Table 6.1: Some XPS data for Co and Co oxides

	OS	Coord	BE	Δ	Satellite	Ref
Co metal			778.0			6.4
			778.2			6.5
			778.2			6.11
			778.2			6.13
			778.2			This Work
CoO	2+	Oct	780.0	2.0	✓	6.4
			780.4	2.2	✓	6.5
			781.1		6.2	6.7
			780.5	2.3	8.2	6.11
Co ₃ O ₄	3+	Oct	779.3	1.1		6.5
	2+	Tet	780.4	2.2	✓	6.5
	2+/3+		780.3		9.5	6.7
	3+	Oct	779.6	1.4		6.11/2
	2+	Tet	780.7	2.5	11.3	6.12
Co ₂ O ₃ *	3+	Oct	779.9	1.9		6.4

OS=Oxidation State

Coord=Coordination Geometry, Oct=Octahedral, Tet=Tetrahedral

BE=Binding Energy of 2p_{3/2} (eV)

Δ =Chemical shift relative to Co metal (eV)

Satellite=Strongest satellite shift (eV) relative to main 2p_{3/2} intensity, ✓ indicates satellite lines are present but no binding energy given

* In all respects, identical to the spectra of Co₃O₄ shown by other authors. Suggested by Brundle *et al*^{6.11, 6.12} that it is doubtful that spectra are actually those of Co₂O₃.

In CoO, the Co (II) atom is octahedrally co-ordinated. The electronic configuration of the Co (II) in CoO is $t_{2g}^5 e_g^2$ (high-spin). CoO is a Mott insulator in which, although the d band is not full, the transfer of a d electron to an adjacent site according to,



is prohibited by the magnitude of the 3d-3d correlation energy U (ie, $U > W$ where W is the bandwidth).

In Co_3O_4 , which is a semiconductor, two-thirds of the Co atoms are in a Co (III) state occupying octahedral sites, whilst one-third are in the Co (II) form and occupy tetrahedral sites (spinel structure). The Co (III) ions have t_{2g}^6 (low-spin - diamagnetic) configuration whilst the Co (II) ions in Co_3O_4 have a $e^4 t_{2g}^3$ (paramagnetic) configuration^{6,17}.

The closed shell configuration ($S=0$) of the Co (III) species in Co_3O_4 means that the corresponding main 2p line is narrower than for CoO. The 2p lines in Co_3O_4 show Co (II) (Tet) species as 'shoulder' peaks to the *higher* binding energy side of the main Co (III) intensity. Several authors have decomposed the Co:2p_{3/2} peak into components due to Co (II) and (III) (see table 6.1). The measurement of the Co:2p spectrum of Co (III) in Co_2O_3 , which contains just Co^{3+} , has been attempted^{6,4, 6.5} but in all cases identical spectra to those of Co_3O_4 result and it was commented later^{6,11} in similar attempts to measure the true spectrum of pure Co (III) oxide, that the surfaces always turn out to be Co_3O_4 . The identification of the XPS binding energy of Co III has been aided by measurement of pure Co (II) and (III) in octahedral and tetrahedral environments in mixed valence Co spinels such as CoFe_2O_4 (Co^{2+} oct.), CoAl_2O_4 (Co^{2+} tet.) and ZnCo_2O_4 (Co^{3+} oct.)^{6,7}.

It is interesting to note that the reported binding energy of Co:2p core-levels is *less* for Co^{3+} than Co^{2+} , the reverse of usual trends. Whilst such behaviour is unusual, it has also been observed in other systems, for example, Pb, PbO and PbO_2 ^{6,18}. Such a situation may arise as a combination of three effects; initial state charge, final state relaxation and Madelung potential considerations. Increasing initial state charge will

increase binding energy, but both the latter terms may lower the apparent binding energy and so must be considered important in Co_3O_4 . Extra-atomic relaxation will be expected to be greatest in Co metal, where electrons from the valence band can screen out d-hole charge. The redistribution of negative charge from neighbouring atoms lowers the energy of the hole state and hence lowers the measured binding energy.

6.6.3 Satellite Structure in Co Oxides

It has been shown^{6.19, 6.20} that high-spin Co (II) compounds have intense satellite structure associated with them whilst in low-spin Co (III) compounds, satellite structure is very weak. Satellite intensity is also present in high-spin Co (III) compounds and it has been argued that it is the presence of unpaired electrons in high-spin Co (III) that allows the appearance of strong photoelectron satellites^{6.21}.

However, the most widely accepted model^{6.22} for the intense satellite structure associated with many of the oxides of late row transition metals (but not d^{10} configuration) takes a somewhat different view. Consider first CoO. The nominal initial d electron configuration is $< 3d^7 |$, but due to covalency this is mixed with a nearly-degenerate $< 3d^8 \bar{L}^1 |$ configuration[‡]. The final states produced with a core hole present will thus depend on the core hole-3d Coulomb interaction Q . If this is greater than the 3d bandwidth W then a state is pulled out of the 3d band and the XPS spectrum contains two regions corresponding to an occupied ($\bar{L}^1$) or empty ($\bar{L}^0$) bound state. In the 2p ionised final state of CoO, the screened/ $2p^5 3d^8 \bar{L}^1 >$ configuration lies below the unscreened/ $2p^5 3d^7 \bar{L}^0 >$ configuration. The former peak appears as the 'main intensity' whilst the latter constitutes the 'satellite structure' at higher binding energy (although it still constitutes a major part of the total 2p intensity).

In low spin Co (III), the increased Co-O covalency gives greater weight to the $3d^7 \bar{L}^1$ ligand hole configuration which lies below the nominal $3d^6 \bar{L}^0$ configuration, even in the initial state. Thus, on photoionisation the system proceeds smoothly to a screened final state configuration without the

[‡] The bar notation is used to represent the presence of holes. $\bar{L}^1$ corresponds to one ligand hole, $\bar{L}^0$ represents no ligand holes and similarly for core holes $\bar{2p}^1$ etc.

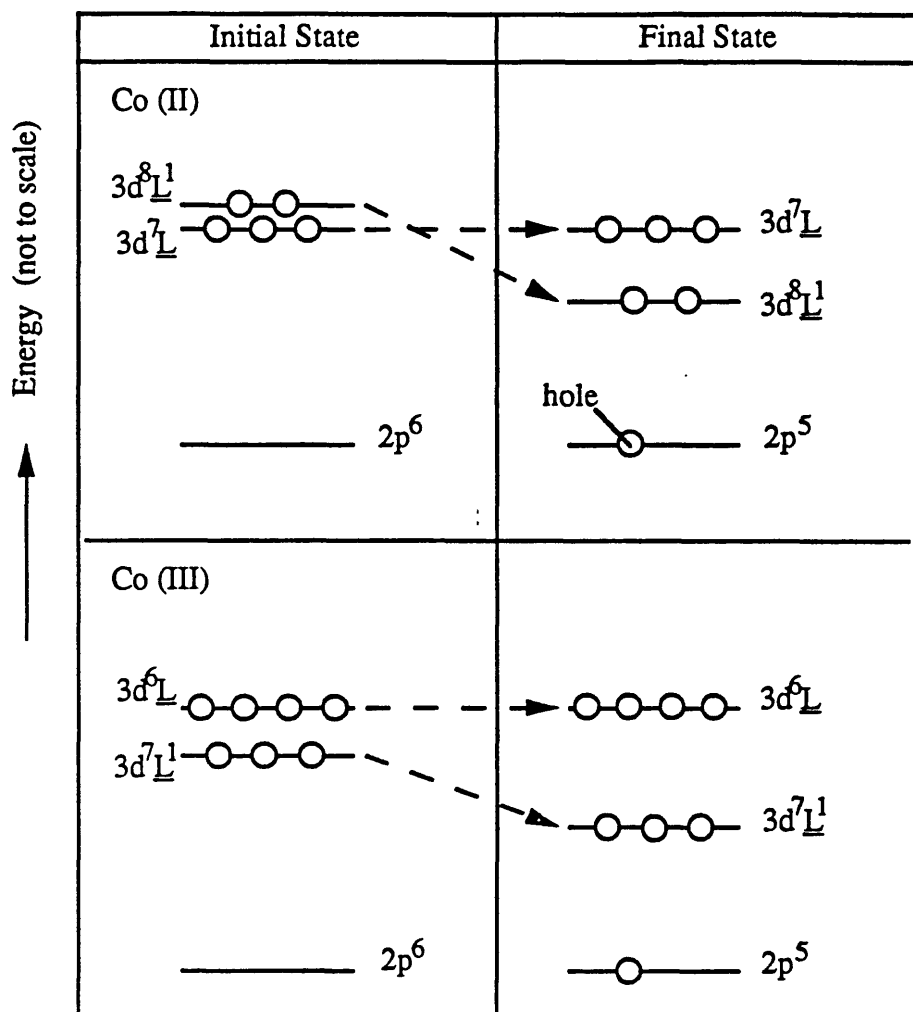


Figure 6.14: In CoO, the nominal initial d electron configuration is $< 3d^7 \underline{L}^1$, but due to covalency this is mixed with a nearly-degenerate $< 3d^8 \underline{L}^1$ configuration. Core ionisation can pull a state out of the 3d band and two final states, corresponding to an occupied ($\underline{L}^1$) or empty ($\underline{L}^0$) bound state, result. In the 2p ionised final state of CoO, the screened/ $2p^5 3d^8 \underline{L}^1$ configuration lies below the unscreened/ $2p^5 3d^7 \underline{L}^0$ configuration. The former peak appears as the 'main intensity' whilst the latter constitutes the 'satellite structure'. In Co (III), the increased Co-O covalency gives greater weight to the $3d^7 \underline{L}^1$ ligand hole configuration which lies below the nominal $3d^6 \underline{L}^0$ configuration, even in the initial state. Thus, on photoionisation the system proceeds smoothly to a screened final state configuration without the appearance of strong $\underline{L}^0$ satellites.

appearance of strong L^0 satellites. The process is illustrated diagrammatically in figure 6.14.

6.7 The Oxidation of Annealed CoTi

6.7.1 The Co Component

The failure to find chemically shifted structure in the Co:2p envelope of oxidised CoTi indicates that the cobalt component of the alloy remains in a zero valence state throughout. Our data do not allow us to discriminate between the possibilities of formation of cobalt metal as a distinct phase or the formation of a Ti-depleted alloy phase.

However, there is some change in the intensity of the 2p peaks relative to the background intensity. The background to the low kinetic energy side of a core photoelectron peak contains contributions from both intrinsic and extrinsic processes. As commented in chapter 2, the latter arise from inelastic scattering processes as photoelectrons propagate to the surface^{6,23}. Thus the extrinsic inelastic background intensity depends on the depth distribution of the photoemitting atoms. For example, if atoms are restricted to the topmost atomic layers of the sample (complete segregation), the background intensity will be lower than for a uniform depth distribution of atoms in some matrix. By measuring the Co:2p_{3/2} height with respect to background intensity at (say) 785eV, the 2p intensity becomes attenuated as oxidation proceeds as shown in figure 6.15. Increased background intensity to the high binding energy side of the Co:2p peak of oxidised Co (but away from the satellite structure) suggests that the Co photoelectrons originate from deeper within the solid than before oxidation, that is, that Co is buried by the Ti-oxide overlayer as oxidation proceeds.

6.7.2 Oxygen Induced Ti Segregation in CoTi

The XPS intensities of the Co:2p, Ti:2p and O:1s peaks (after correction by suitable sensitivity factors) with oxygen exposure are shown in figure 6.16. When measured at 90° take-off angle, there is a continuous decrease of the Co:Ti ratio with oxidation and after 7500L O₂ an XPS intensity ratio of Co:Ti=0.95 indicates a surface stoichiometry of

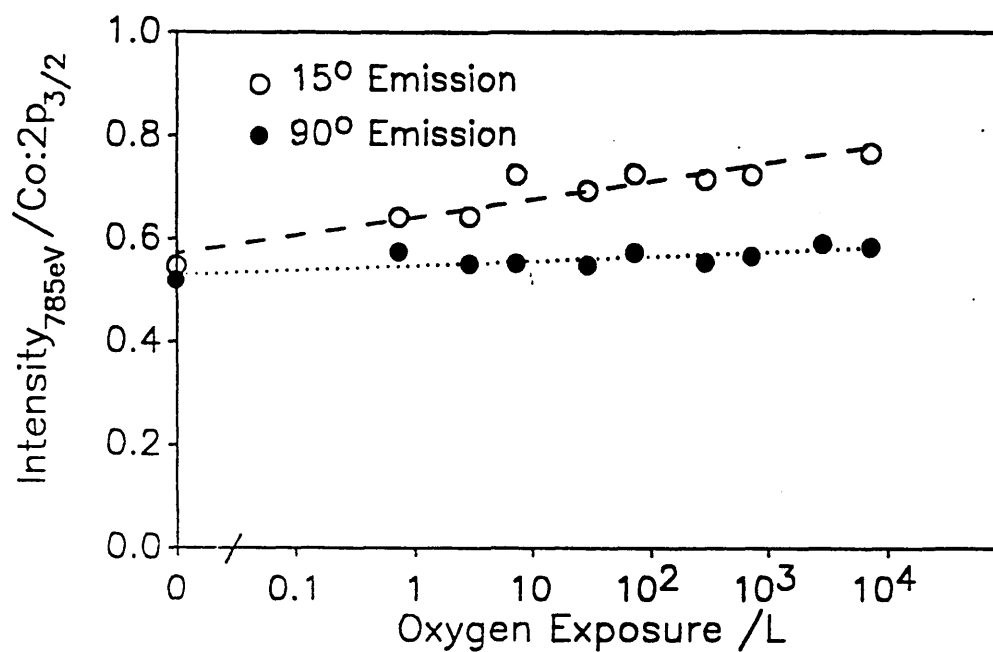


Figure 6.15: Intensity of inelastic background (at 785eV) versus Co:2p_{3/2} height in Co:2p spectra of annealed CoTi with oxygen exposure. An increase in background is indicative of burying of Co atoms as oxidation proceeds.

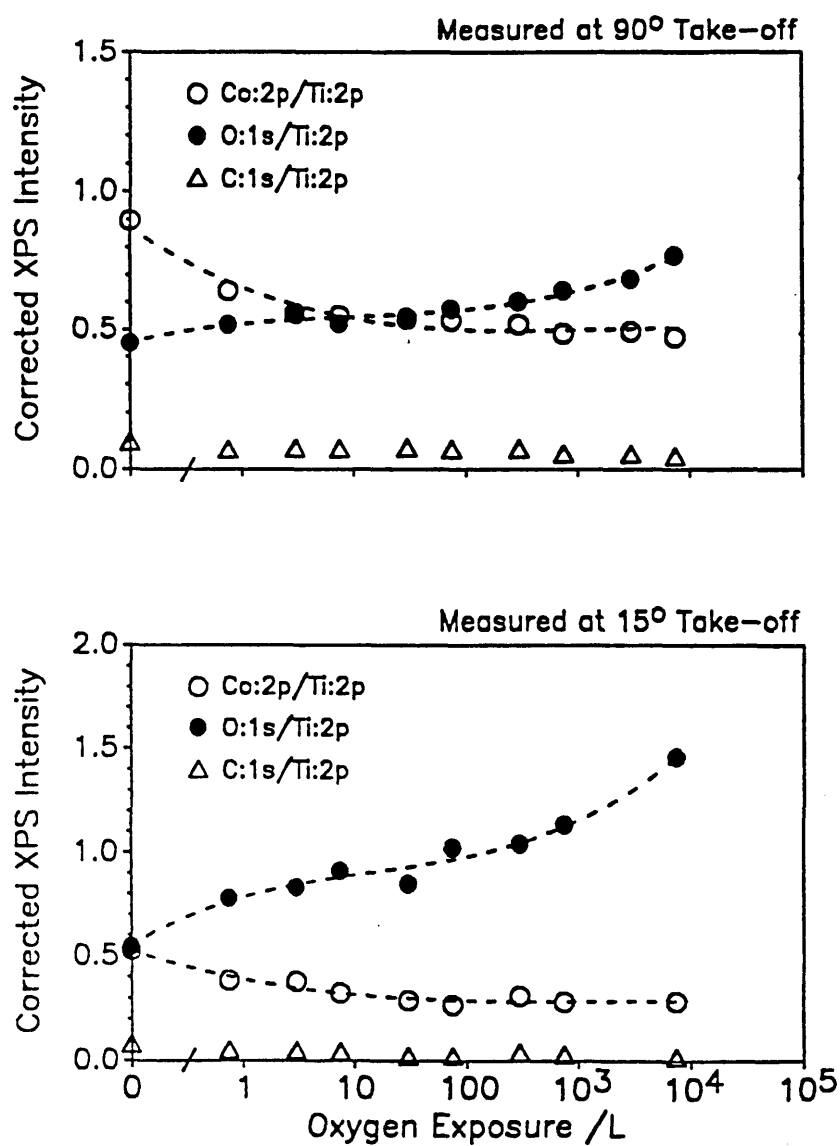


Figure 6.16: Variation in Co:2p, O:1s and C:1s peak intensity ratios (corrected for sensitivity factors) relative to Ti:2p from normal and grazing emission Mg XPS for O₂ on annealed CoTi.

approximately $\text{Co}_{0.45}\text{Ti}$ confirming that segregation of Ti atoms is induced by oxidation. The O:1s intensity increases continuously with exposure.

If measured at 15° grazing take-off angle, the oxygen induced surface segregation of Ti appears to proceed at a slower rate, although the Ti concentration at the extreme surface is initially much enhanced over the 90° data before any oxidation. If the photoelectron pathlength for Co:2p photoelectrons is estimated at $12\text{\AA}$, then attenuation of intensity by a factor 100 (approximately the limit of detectability) occurs for photoelectrons emerging from about $60\text{\AA}$. This is reduced to only $15\text{\AA}$ if measured with 15° take-off emission. The O:1s signal relative to the total metal intensity increases more rapidly in this instance. After 7500L O_2 the surface stoichiometry under these conditions was approximately $\text{Co}_{0.25}\text{Ti}$ but is roughly constant from 30→7500L O_2 .

6.7.3 Spectral Subtraction and Curve Fitting the Ti:2p Spectra

Figure 6.17 shows a comparison between the Ti:2p_{3/2} structure of clean Ti foil and annealed CoTi. The measured binding energy of the Ti:2p_{3/2} peak of CoTi at normal emission is at 455.1eV, higher than expected for metallic Ti. The peak is also broadened in the alloy. The exact location of this peak is variable between 454.7eV and 455.3eV, depending on the O content of the annealed surface, although the position of the Co:2p peaks remain constant. This is an indication that the Ti:2p structure of annealed CoTi may be made up of two superimposed doublets, one due to metallic Ti (0) in the alloy and one associated with the irreducible oxide. By simply varying the relative abundance of the oxide species, it should be possible to simulate the shift in the observed 2p peak binding energy.

However, attempts to synthesise the Ti:2p_{3/2} region of CoTi using the previously defined peak position and shape for Ti metal and a variable component chemically shifted +1.8eV^{6.24} to represent titanium monoxide, it was impossible to construct a spectrum similar to that experimentally determined. The inclusion of further components to represent Ti (III) and Ti (IV) oxides did not improve the fit of the data.

Figure 6.18 shows the spectral subtraction of the scaled Ti:2p region

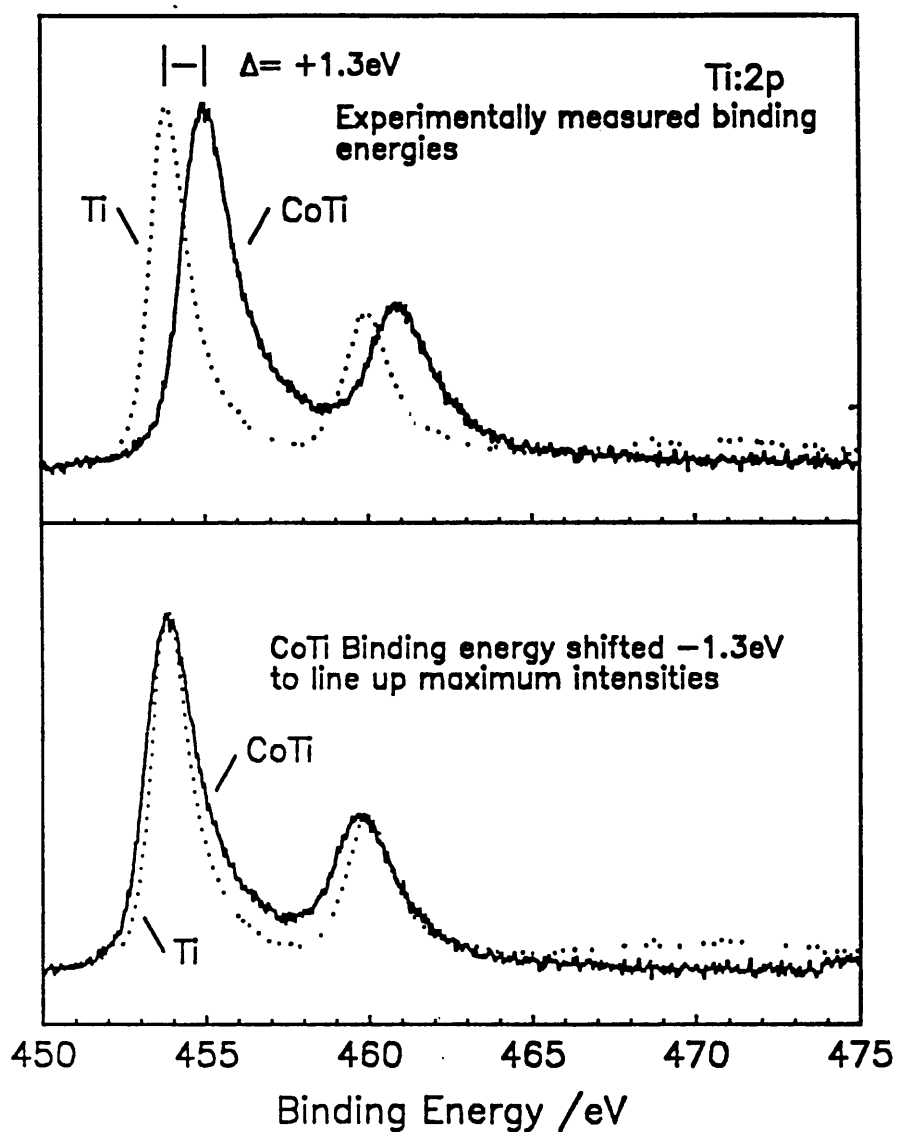


Figure 6.17: Comparison between the Ti:2p spectra of Ti metal (dotted line) and CoTi (solid line). In the top panel, the spectra are presented on same binding energy scale, highlighting the shift of +1.3eV of the CoTi Ti:2p peaks. In the lower panel, the two spectra have been brought into coincidence at the $2p_{3/2}$ peak maximum and shows the broader 2p peaks of CoTi.

of unexposed minus O₂ exposed annealed CoTi, measured at 15° emission angle. After exposure to only 0.75L O₂, a considerable change is observed in the spectrum, characterised by loss in intensity at 454.5eV. It is important to note that the position of maximum loss is constant at this value for all exposures up to 7500L O₂. Figure 6.19 shows similar spectral subtractions for data measured at 90° emission angle. Again, loss in intensity occurs at 454.5eV binding energy, even for exposures as low as 0.75L O₂. After 3L exposure, structure appears at 455.5→459eV and similar growth occurs throughout this region up to 75L when growth is concentrated around 459eV binding energy. Gains in intensity at ≈459eV then dominate from 300 to 7500L O₂.

Also shown in the figure is Ti:2p difference data obtained when Ti metal was exposed to 7500L O₂ (figures 6.19(j)). Whilst the spectra are at first sight qualitatively very similar to the difference data of CoTi, and maximum intensity growth occurs at almost exactly the same energy (458.8 cf 459.0eV), careful comparison demonstrates that the position of maximum intensity loss is shifted 0.7eV to higher binding energy in the CoTi Ti:2p spectrum. Similar, although less pronounced, changes are observed at normal emission. The region of maximum intensity loss undoubtedly corresponds with a decrease in the metallic Ti component of the surface as oxide concentration increases with oxygen exposure.

As a result, the Ti:2p region can be successfully synthesised as shown in figure 6.20 assuming binding energies of 454.5eV for metallic Ti⁰:2p_{3/2} and a chemical shift of only 0.9eV for Ti→Ti²⁺ (of the order of experimental resolution), positioning the Ti²⁺:2p_{3/2} peak at the same value of 455.4eV as that found in the oxidation of Ti metal (see chapter 4). Thus we can assign the irreducible oxide as TiO-like. By changing the Ti⁰/Ti²⁺ ratio, the variability of the initial peak position can be reproduced together with the unusual 2p shape and increased peak width when compared to Ti metal.

6.7.4 Characterisation of Oxides on Annealed CoTi

To characterise the chemical changes to the Ti component of annealed CoTi with oxidation, a reconsideration of the spectral subtraction results is necessary.

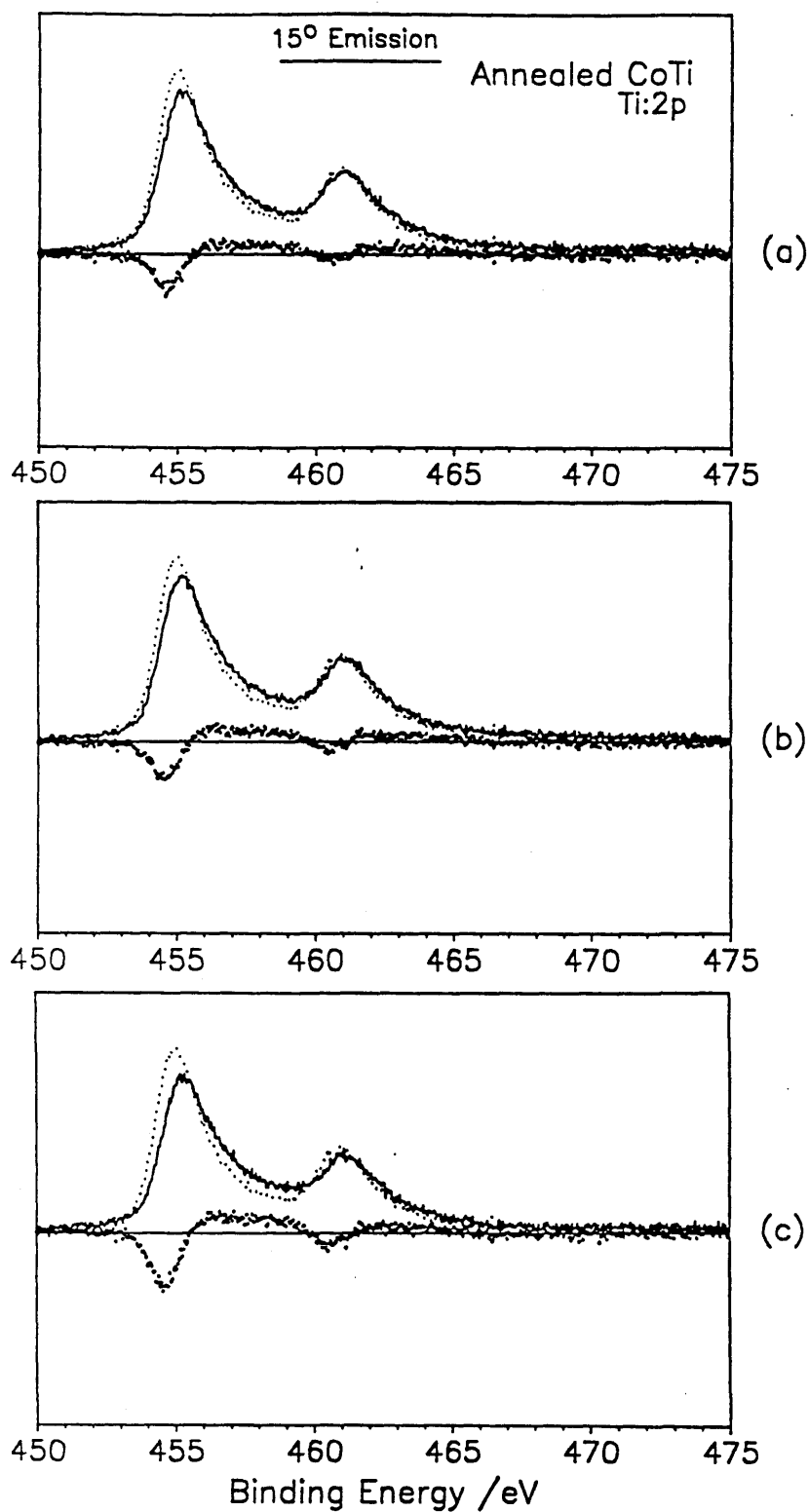


Figure 6.18: Mg $K\alpha_{1,2}$ Ti:2p spectra measured at 15° take-off angle for annealed CoTi with exposure to O_2 . Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots (a) 0.75L (b) 3L (c) 7.5L O_2 . A suitable inelastic background has been subtracted.

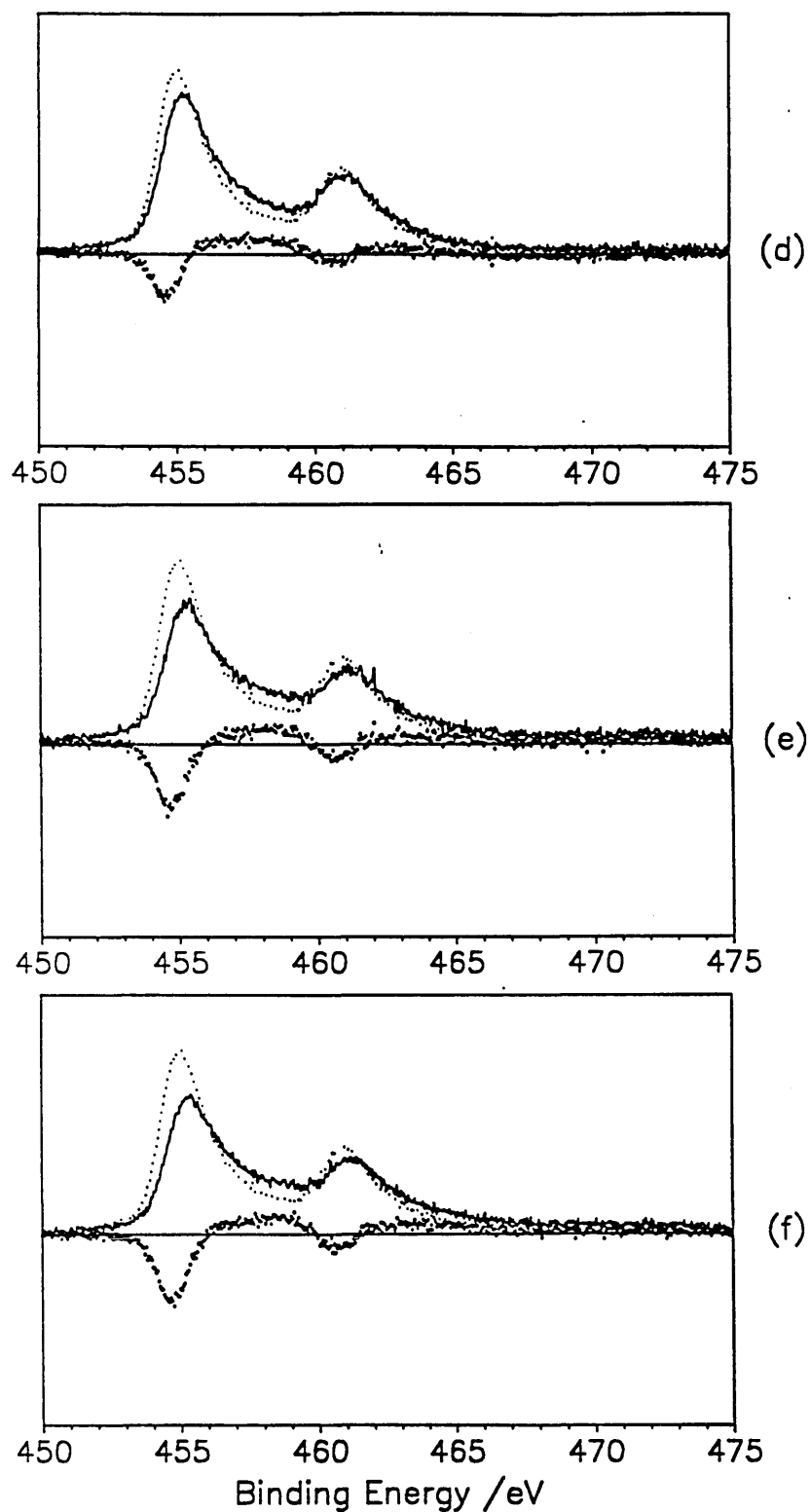


Figure 6.18 (continued): Mg $K\alpha_{1,2}$ Ti:2p spectra measured at 15° take-off angle for annealed CoTi with exposure to O_2 . Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots (d) 30L (e) 75L (f) 300L O_2 .

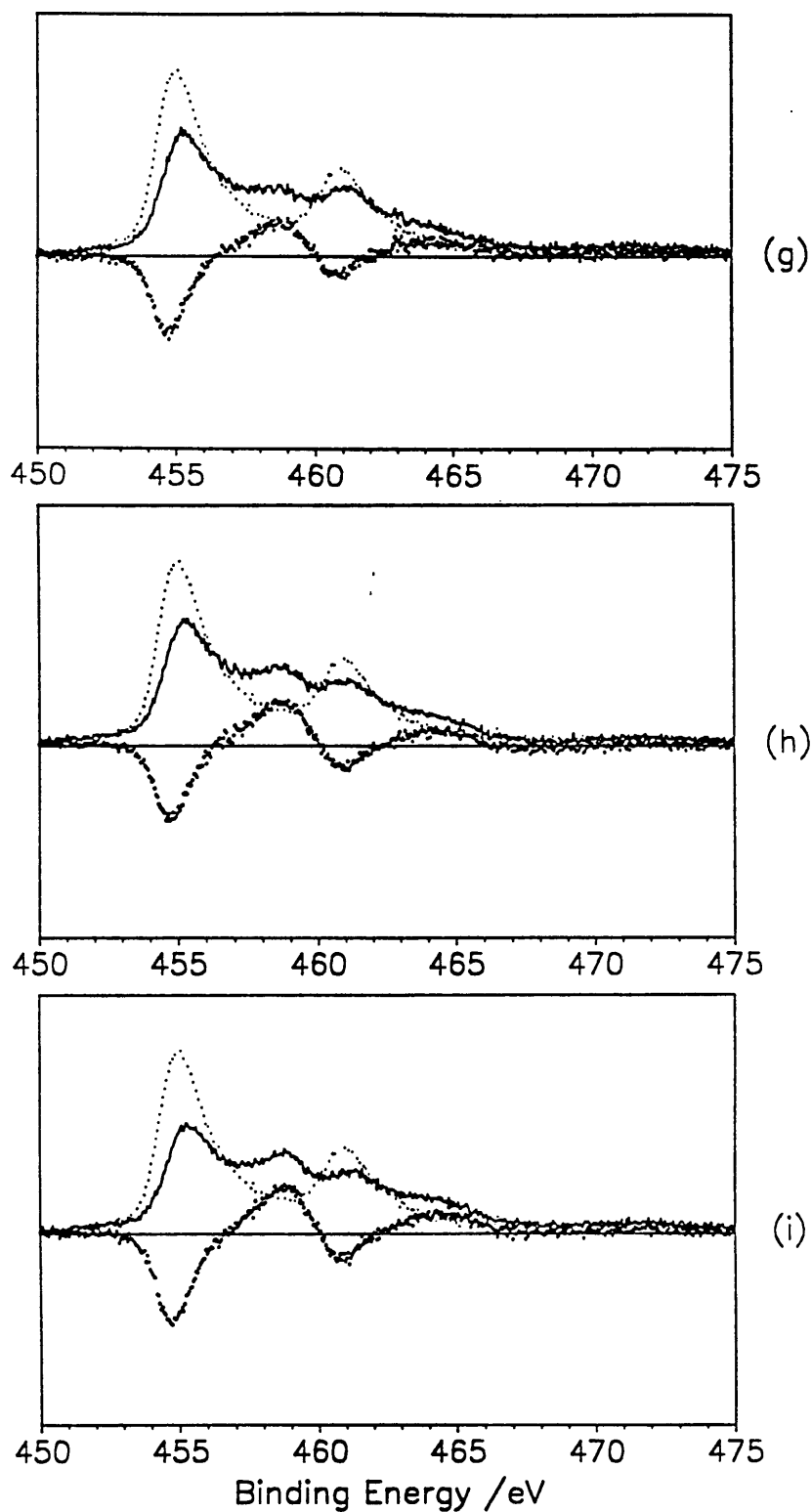


Figure 6.18 (continued): Mg K $\alpha_{1,2}$ Ti:2p spectra measured at 15° take-off angle for annealed CoTi with exposure to O₂. Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots (g) 750L (h) 3000L (i) 7500L O₂.

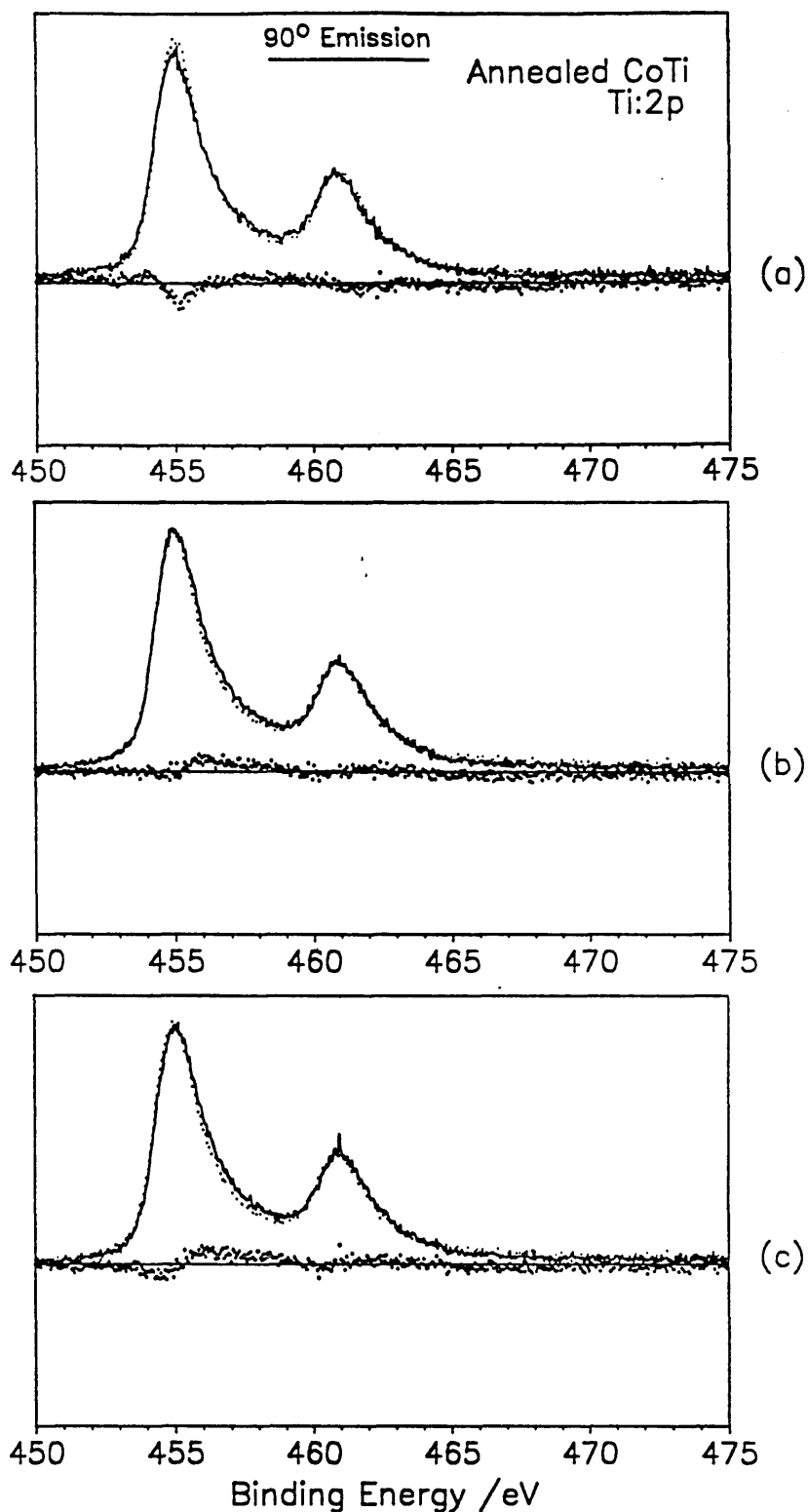


Figure 6.19: Mg $K\alpha_{1,2}$ Ti:2p spectra measured at 90° take-off angle for annealed CoTi with exposure to O_2 . Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots (a) 0.75L (b) 3L (c) 7.5L O_2 . A suitable inelastic background has been subtracted.

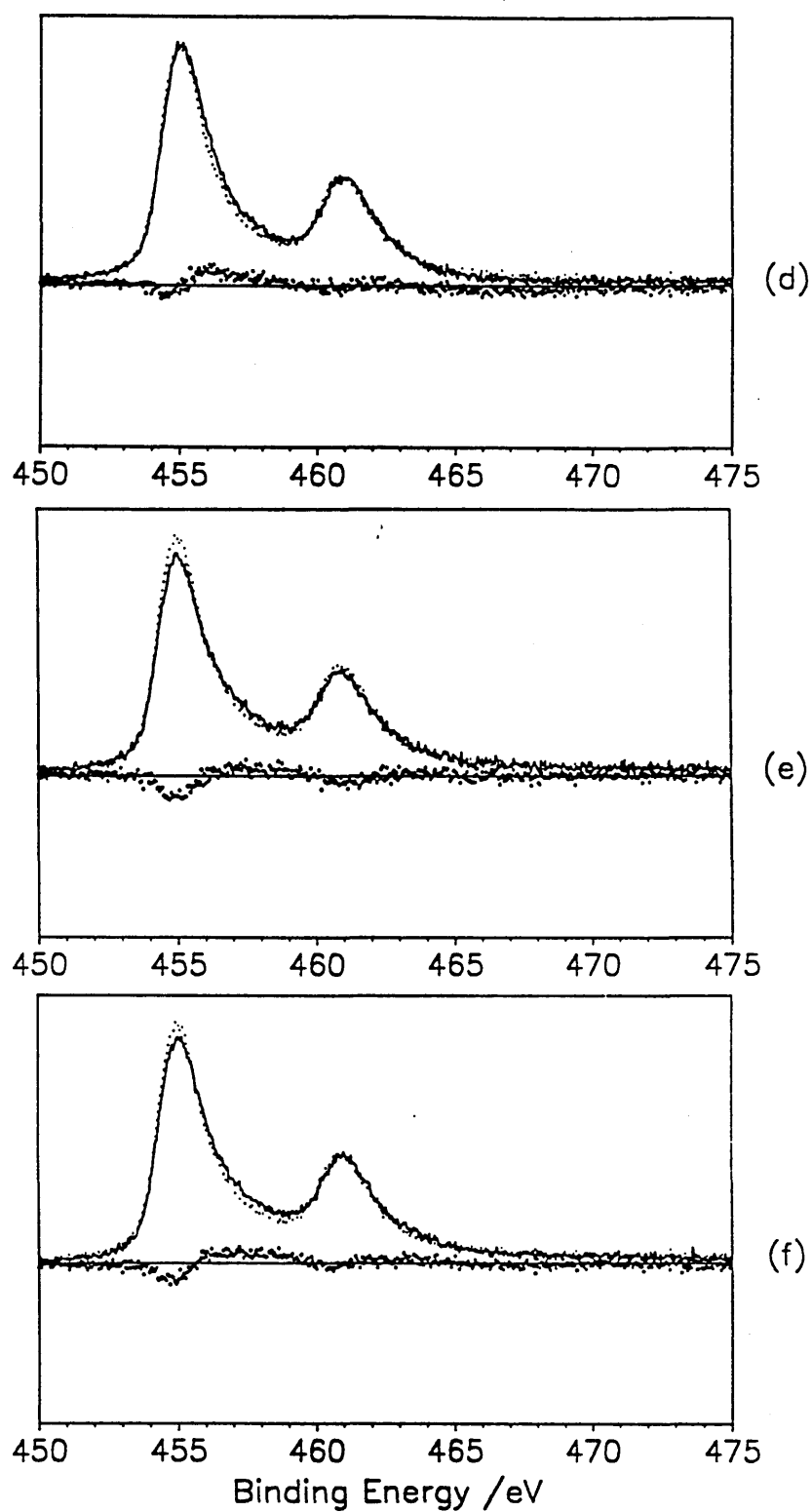


Figure 6.19 (continued): Mg $K\alpha_{1,2}$ Ti:2p spectra measured at 90° take-off angle for annealed CoTi with exposure to O_2 . Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots (d) 30L (e) 75L (f) 300L O_2 .

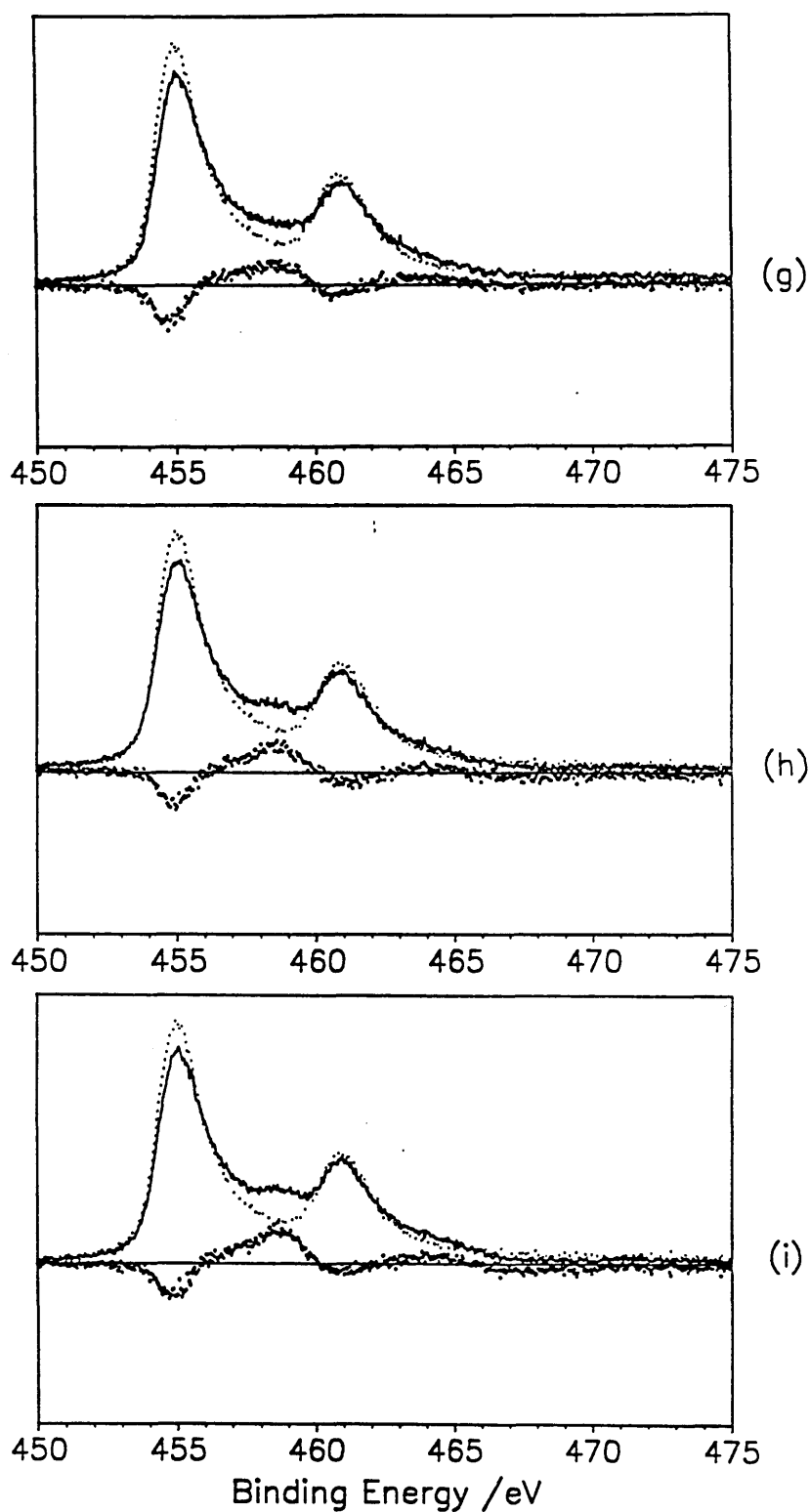


Figure 6.19 (continued): Mg $K\alpha_{1,2}$ Ti:2p spectra measured at 90° take-off angle for annealed CoTi with exposure to O_2 . Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots (g) 750L (h) 3000L (i) 7500L O_2 .

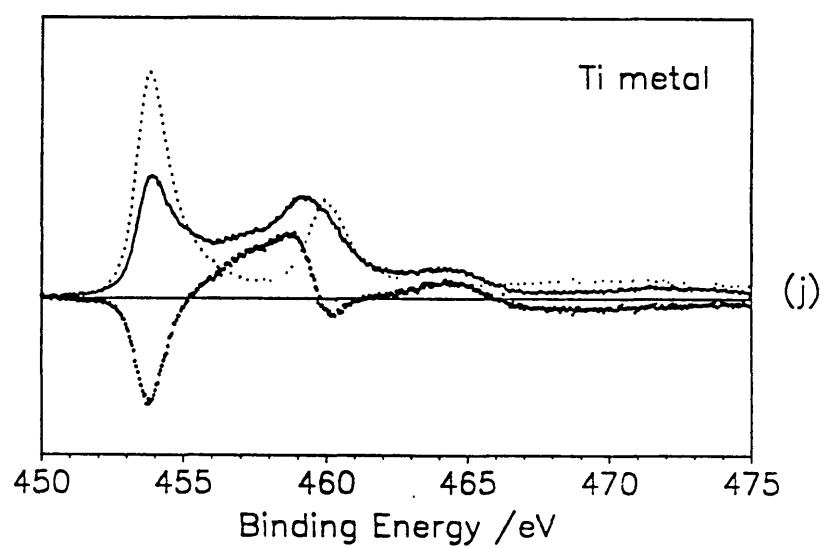


Figure 6.19 (continued): (j) Mg $K\alpha_{1,2}$ Ti:2p spectra measured at 90° take-off angle for Ti metal exposed to 7500L O₂. Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots.

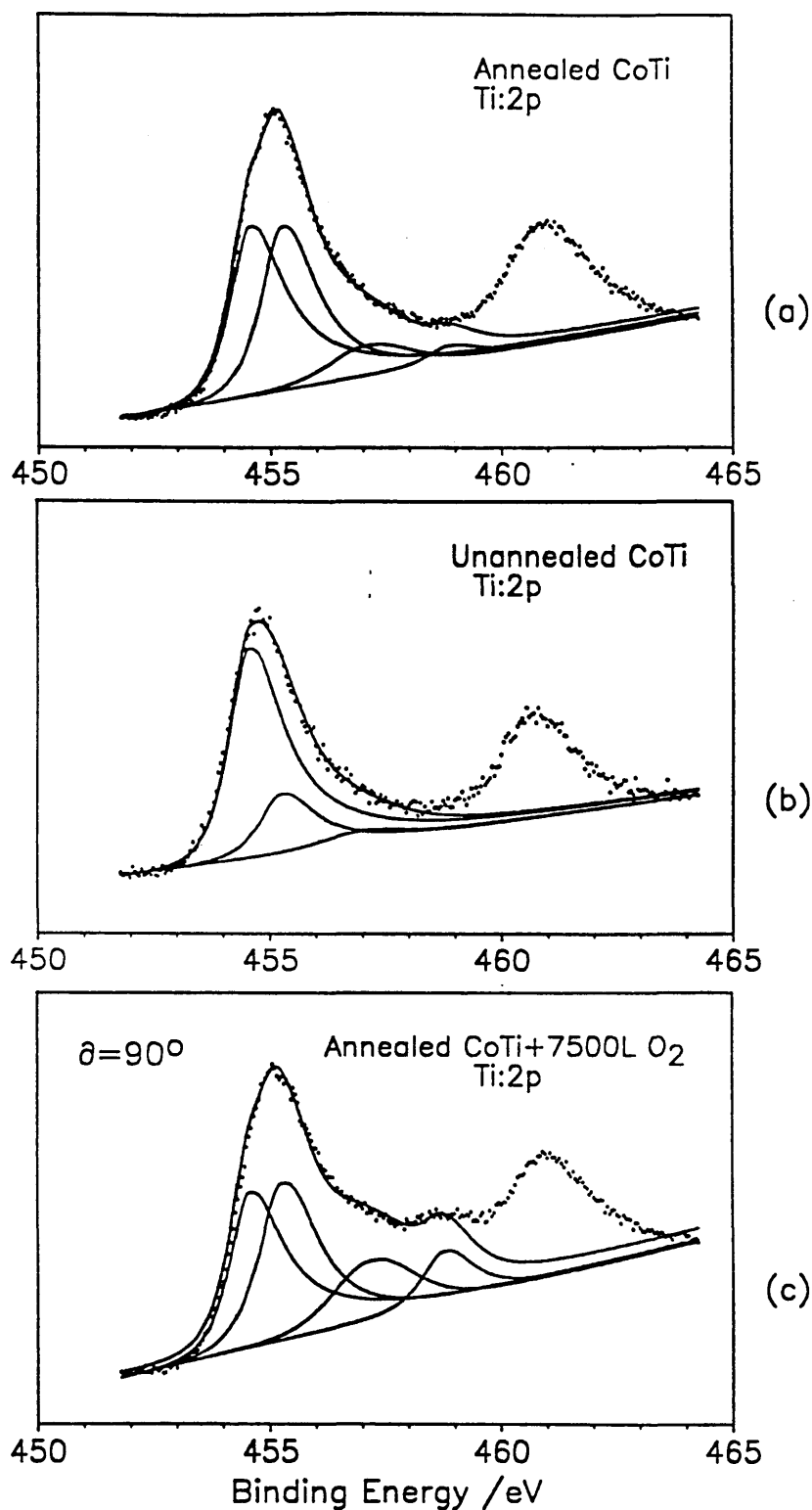


Figure 6.20: Examples of curve fitting (solid line) to Ti:2p spectra (dots) for CoTi (a) annealed CoTi (b) sputtered CoTi and (c) annealed CoTi plus 7500L O₂. The four component peaks represent Ti (0), Ti (II), Ti (III) and Ti (IV) oxide in increasing binding energy. The position of each peak is based on literature^{6.24}.

Consideration of the shallow emission angle data shows that at low exposures (<3L O₂) an attenuation in intensity located at 454.5eV occurs relative to intensity between $\approx$ 456 and 459eV (figure 6.18). Intensity growth is concentrated at $\approx$ 456eV. At higher exposures, the attenuation is more marked and above 30L intensity growth begins to concentrate around 459eV. The growth of a chemically shifted spin-orbit Ti:2p doublet is readily apparent in these spectra before new spectral peaks are resolved in the 'raw' data. These features persist up to 7500L, when it is clear that intensity has grown throughout the 456-459eV region but that the greater chemically shifted component is dominant. The new doublet continues to grow in intensity up to the highest exposure.

The chemical shift of the new spectral feature relative to the unoxidised Ti:2p_{3/2} peak is $\approx$ +3.7eV binding energy. This shift corresponds to that seen by Carley *et al*^{6.24} and Armstrong and Quinn^{6.25} in the early stages of Ti metal oxidation and attributed to a Ti³⁺ oxide (Ti₂O₃). Indeed, the O:Ti ratio of 1.45 after 7500L O₂ estimated from the XPS data gives a stoichiometry close to that expected for Ti₂O₃. There is no indication in the difference data for the formation of a species chemically shifted by 5.1eV (Ti⁴⁺) from the original peaks. Based on chemical shift information alone, it is tempting to assign the shifted 2p peaks as due to a Ti³⁺ oxide. Indeed, lining up the two initial 2p_{3/2} peaks for CoTi and Ti produces almost perfect correlation between the Ti (III) peaks of oxidised Ti and the dominant peaks observed in the oxidation of CoTi.

However, a further consideration of the data suggests that this is an incorrect conclusion. Firstly, the growth of the new 2p_{3/2} peak at 458.8eV corresponds very closely with the 459.0eV binding energy given in various literature and found here associated with Ti⁴⁺ (TiO₂). Once a Ti atom begins to be coordinated by O atoms, Co-Ti interaction is reduced and so the Ti²⁺, Ti³⁺ and Ti⁴⁺ peaks for the respective oxides should occur close to the bulk values. Secondly, the stability of a product Ti₂O₃ surface is highly questionable. An investigation of this oxide has been undertaken^{6.26, 6.27} and it was noted that when Ti₂O₃ is exposed to O₂ it rapidly oxidises to TiO₂. An attempt to produce a clean Ti₂O₃ surface from a stoichiometric powder^{6.28} revealed a thick TiO₂ overlayer. Once prepared, the Ti₂O₃ surface oxidised extensively overnight in UHV conditions.

The assumption that the metallic Ti (0) peak in CoTi is located at an identical binding energy to that in Ti metal is obviously incorrect as discussed further below. In the light of these considerations, the growth of intensity in the raw data at 458.8eV can be assigned as due to a TiO₂-like oxide, but the presence of TiO and Ti₂O₃ is also observed.

6.7.5 Titanium Sub-oxide Concentration

The concentration of each of the sub-oxide components can be estimated by curve fitting the Ti:2p region of CoTi, and examples are shown in figures 6.20. In this way it was possible to estimate the concentration of each of the oxide components in the overlayer. By measuring the intensity at 455.4, 457.1 and 458.8eV (the estimated binding energies of Ti²⁺, Ti³⁺ and Ti⁴⁺ respectively) in the spectral synthesis, figure 6.21 shows as oxidation proceeds there is an initial increase in Ti²⁺ concentration which quickly reaches a limiting value. Both Ti³⁺ and Ti⁴⁺ intensity increases progressively once the Ti²⁺ intensity has saturated. All oxide components are enhanced at shallow emission angles, but the effect is strongest for the Ti⁴⁺ peaks after high oxygen exposure. Thus, one can envisage a structure for the oxide overlayer in which all three oxidation states are present but which is dominated by TiO at low exposure and TiO₂ at high exposure in a similar manner to the oxidation of Ti metal.

6.8 The Oxidation of Sputtered CoTi

The intensities of the O:1s, Ti:2p and Co:2p core levels on unannealed CoTi during oxidation (corrected by sensitivity factors) are shown in figure 6.22. Immediately obvious is the more rapid increase in the O:1s intensity when compared to the annealed surface. This is to be expected, since the sputtered surface will be highly disordered and is likely to contain a large concentration of defect sites, steps and other low coordinate metal atoms.

When compared to the annealed surface, although Ti segregation effects are still observed, an increase in the rate of segregation occurs. This figure also demonstrates the initial oxygen concentration of the unannealed

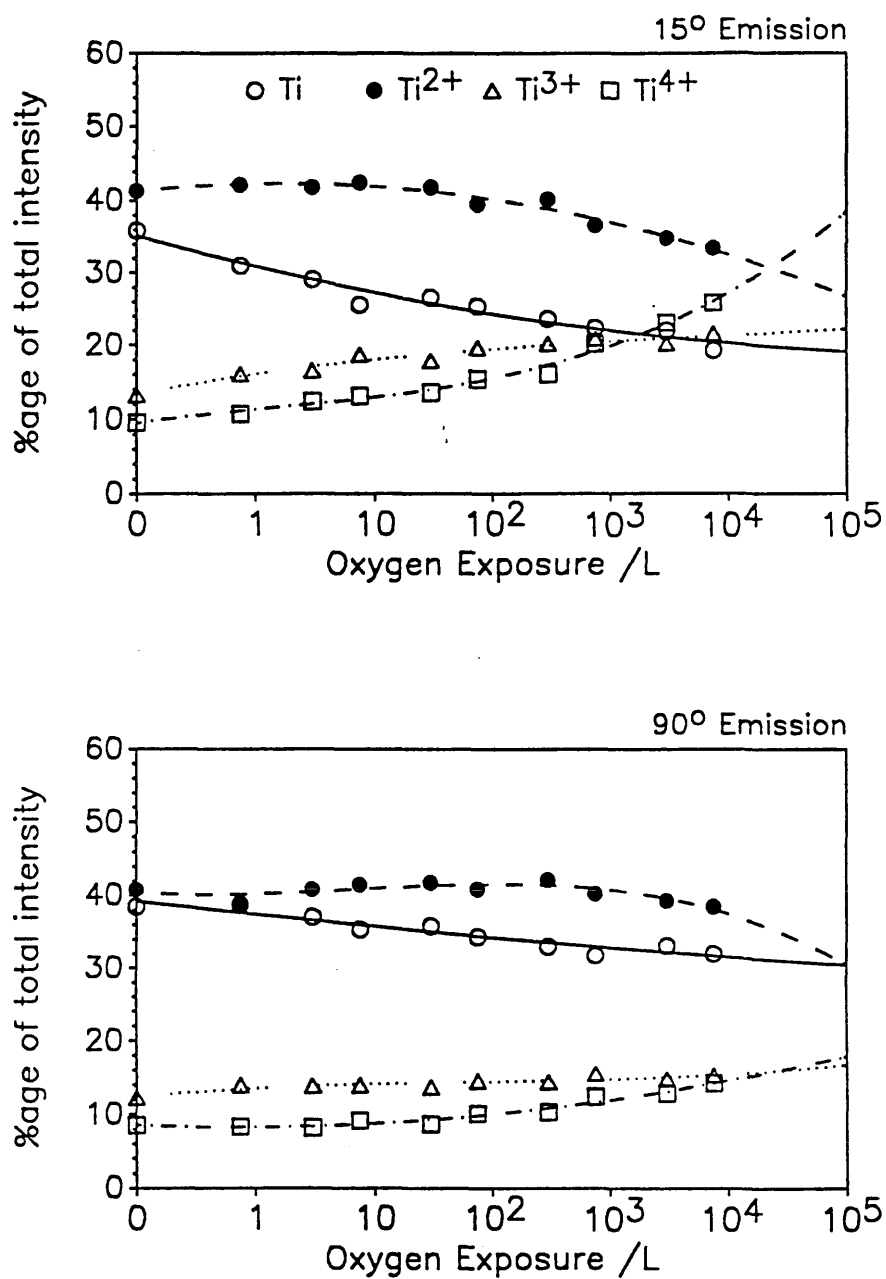


Figure 6.21: Relative concentration of Ti oxides with oxidation. Obtained measurement of intensity of component peaks of curve-fitted Ti:2p region.

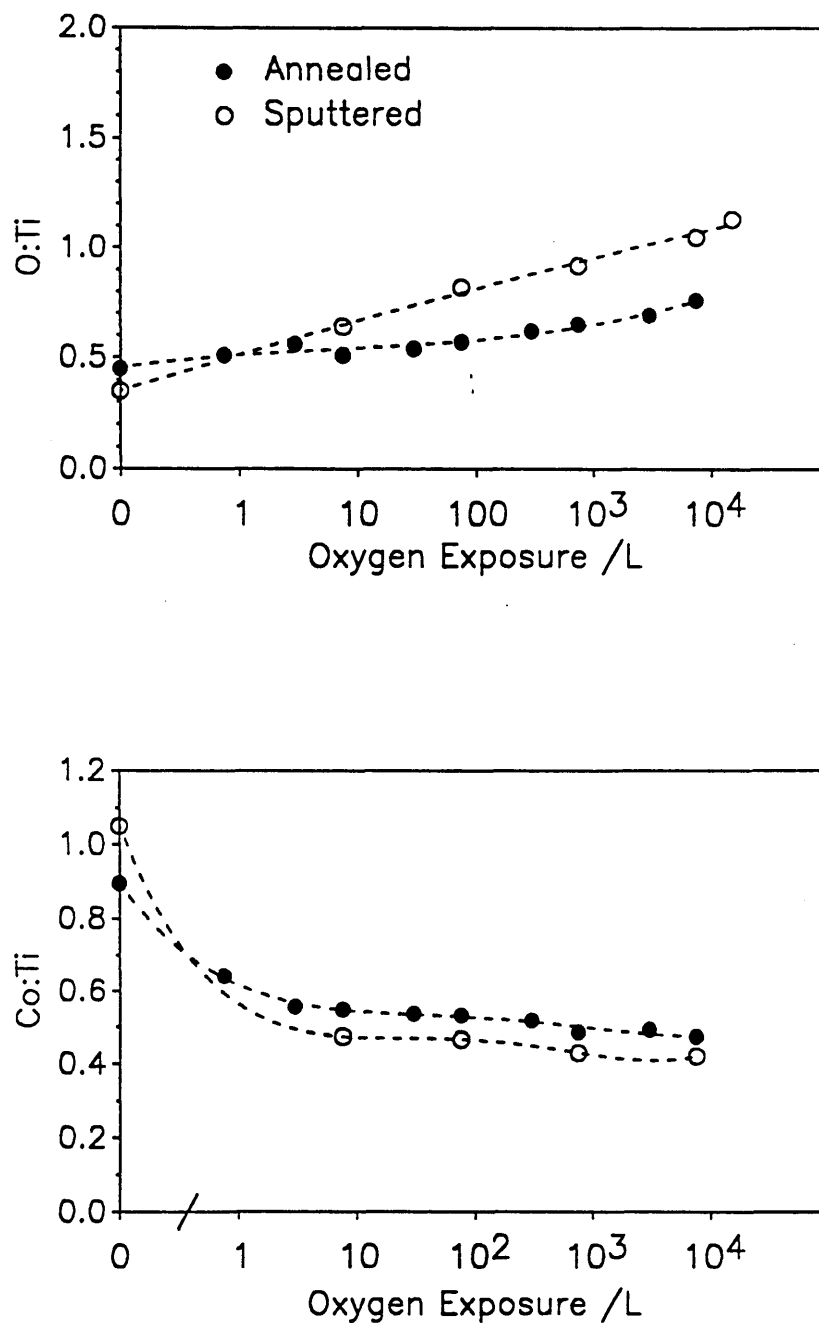


Figure 6.22: Intensity ratios of O:1s and Co:2p relative to Ti:2p for annealed and sputtered CoTi, corrected for sensitivity factors. As oxidation proceeds, The O:1s intensity increases much more rapidly for the sputtered surface when compared to the annealed surface. A decrease in the Co:Ti ratio indicates Ti segregation in both cases.

surface is reduced with respect to the annealed one: an initial O:Ti ratio of 0.34 for the sputtered surface compared to 0.46 for the annealed surface from corrected intensity measurements. The Ti:2p structure of the etched surface clearly show the metallic $\text{Ti}^{0:2p_{3/2}}$ peak located at the value predicted from the annealed surface and vindicates that the Ti (0) component of CoTi is located at $\approx 454.5\text{eV}$. It can be seen clearly as the dominant peak at this binding energy in figure 6.7, whilst the asymmetric peak shape is produced by a relatively minor Ti^{2+} contribution.

Furthermore, by measuring the Ti:2p shape at grazing emission, as in figure 6.23, an increase in the relative contribution of TiO species is obvious in contrast to the relatively uniform distribution of O at the annealed surface. On the sputtered surface, oxygen concentration is greatest in the very top atomic layers and this may indicate some segregation of O.

The construction of appropriately scaled difference spectra was attempted as for the annealed surface, and the results are given in figure 6.24. Qualitatively similar results are obtained: oxidation proceeds in a similar manner to on the annealed alloy. For exposure to 7.5L O_2 , simultaneous growth of Ti^{2+} , Ti^{3+} and Ti^{4+} oxides can be seen. for exposures greater than 7.5L, the dominant oxide formed is TiO_2 -like. It is possible to clearly identify in the difference data, loss in intensity due to metallic Ti and Ti^{2+} , especially at higher O_2 exposures.

6.9 Chemical Shifts in Alloys

A shift in the Ti:2p core level in CoTi of $+0.7\text{eV}$ binding energy, from 453.8eV to 454.5eV , is certainly large with respect to differences in electronegativity of the two components ($\text{Ti}=1.6$, $\text{Co}=1.76^{6.29}$). In the 1960's it was argued that the Fe-Ti, Co-Ti and Ni-Ti bonds in these ordered 1:1 intermetallic compounds contained some degree of covalent character. It was argued that 'quasi-ionic bonding' with electron transfer from Ti to its counterpart atom occurred^{6.30}. Charge transfer was also implied from the calculations of Papaconstantopoulos^{6.31}.

The difference in electronegativity of these transition metals is very much smaller than is typically experienced in, for example, a metal oxide (electronegativity $\text{O}=3.56^{6.29}$). The electronegativity difference in a metal

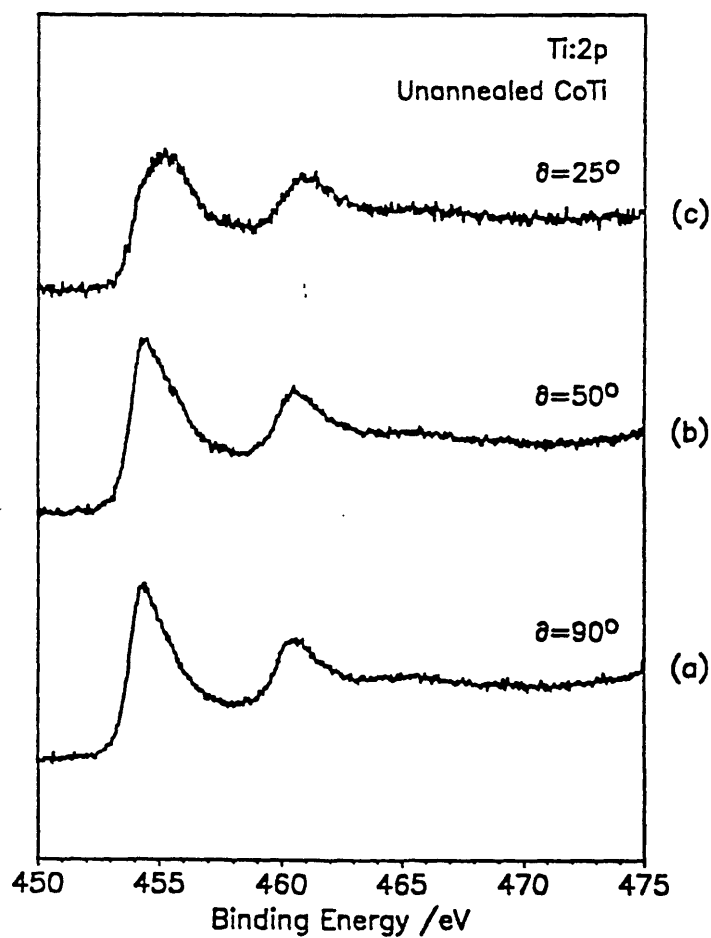


Figure 6.23: Ti:2p region of sputtered CoTi surface measured at different take-off angles θ (a) 90° (b) 50° (c) 25° relative to surface plane.

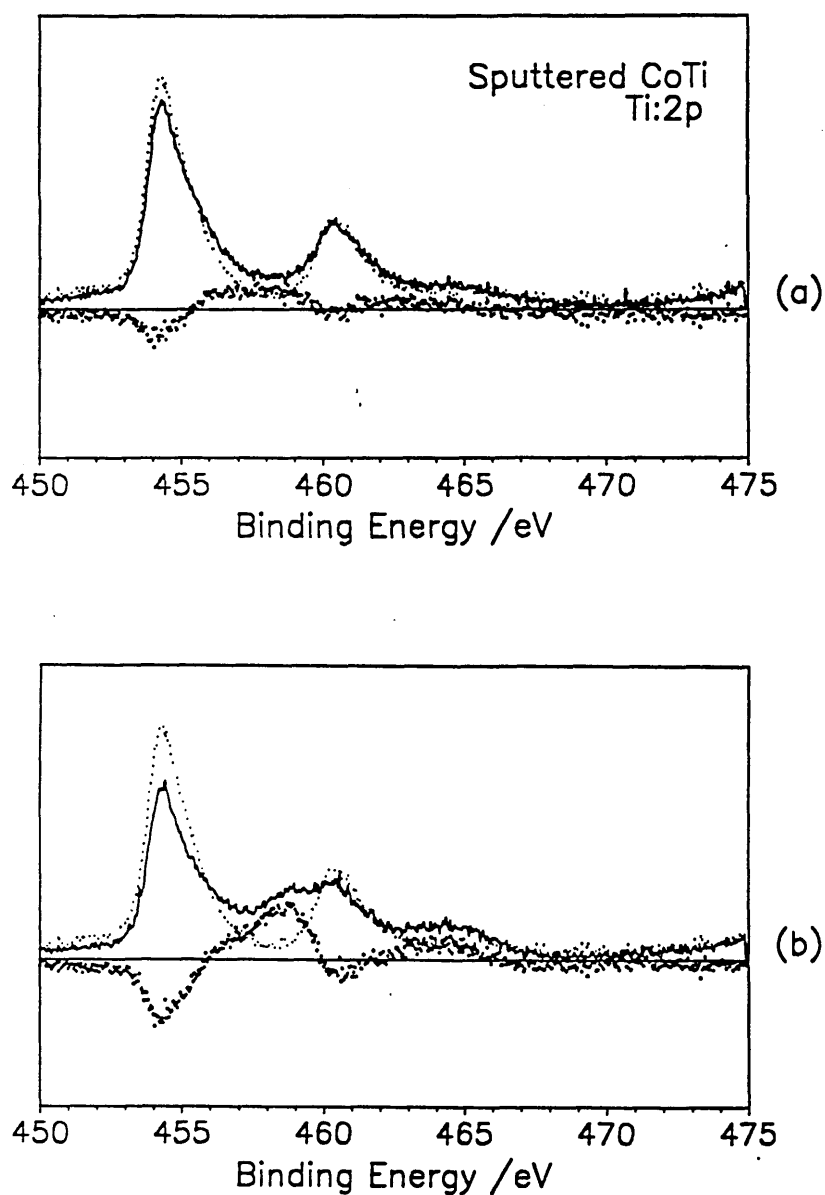


Figure 6.24: Mg $K\alpha_{1,2}$ Ti:2p spectra measured at 90° take-off angle for sputtered CoTi with exposure to O_2 . Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots (a) 7.5L (b) 75L. A suitable inelastic background has been subtracted.

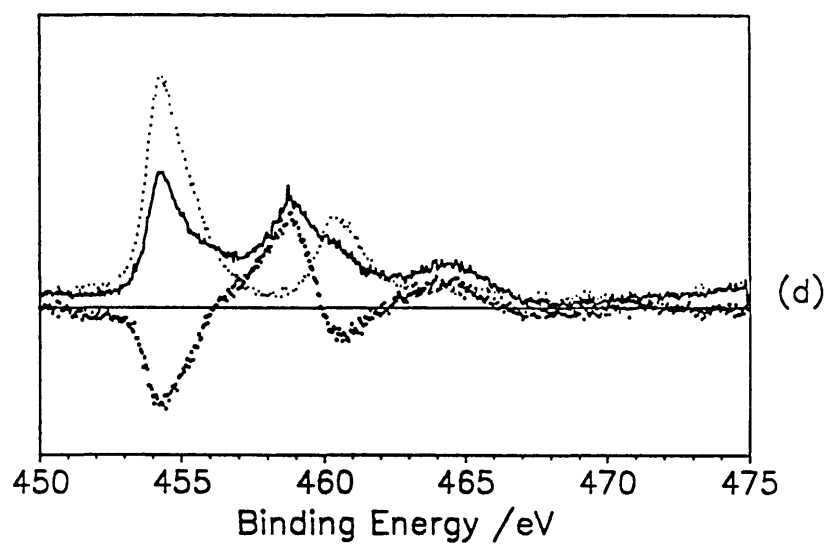
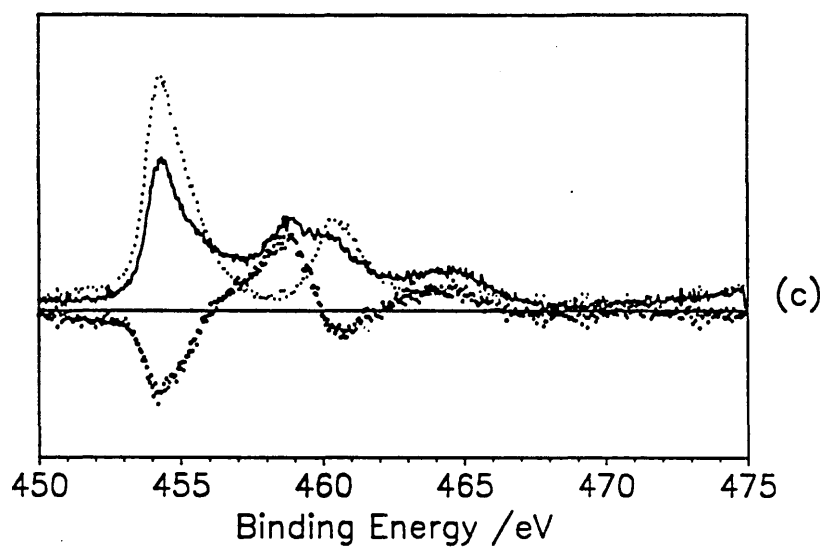


Figure 6.24 (continued): Mg K $\alpha_{1,2}$ Ti:2p spectra measured at 90° take-off angle for sputtered CoTi with exposure to O₂. Unexposed spectrum is shown as light dots, the exposed spectrum as a solid line and the difference data as heavy dots (c) 750L (d) 7500L O₂.

oxide typically gives rise to chemical shifts of a few eV. Furthermore, the Co:2p_{3/2} peaks in Co metal and CoTi are at 778.2eV and 778.4eV respectively ($\Delta=+0.2\text{eV}$), shifted to higher binding energy. If charge transfer between Co and Ti atoms ($\text{Ti}^{\delta+}\text{Co}^{\delta-}$) causes the shifts of the core level peaks of CoTi, the δ^- atom (Co) core peaks should shift to *lower* binding energy whilst the δ^+ (Ti) species to *higher* binding energy. Additionally, the shift will be of the same magnitude for each component. Clearly, some other factor must be accounting for the major part of the peak shifts in CoTi.

The core shifts of NiTi, CoTi and FeTi x-ray lines have been investigated by x-ray emission spectroscopy (XES)^{6.32}. By measuring the energy of the x-ray lines $\text{K}\alpha_1$ ($2\text{p}_{3/2}\rightarrow 1\text{s}$), $\text{K}\alpha_2$ ($2\text{p}_{1/2}\rightarrow 1\text{s}$) and $\text{K}\beta_{1,2}$ ($3\text{p}\rightarrow 1\text{s}$) of these three compounds, shifts to higher binding energy of the Ti lines were found in all three instances. The Ni lines also shifted to higher binding energy in NiTi. No shifts of the Fe or Co lines were observed within the experimental error. It was similarly argued that charge transfer cannot be a major consideration in these compounds, on the ground that both shifts are in the same direction. The shifts were explained by assuming an electron rearrangement (rehybridisation) within the core levels upon bonding. It was calculated that negative XES shifts could only result if 3d electrons are transferred to (not fully occupied) orbitals of 4s character. In this way, the mean radial distribution of the valence electrons is shifted away from the core and the remaining inner electron orbitals contract in the wake of reduced nuclear screening. However, it is difficult to reconcile this argument with the observation of decreased Co:2p satellite structure seen upon alloy formation (see chapter 7).

An alternative basis for explaining core level shifts in alloys is provided by the 'equivalent cores approximation'. Mårtensson *et al*^{6.33} developed a Born-Haber-type model to explain the core level binding energy shifts between free and condensed atoms. The main assumption of the scheme was that the core hole created in photoemission is completely screened by the valence electrons. The core level ionised atom Z is then equivalent to a neutral impurity atom Z+1, and so the core level binding energy should include the heat of solution of atom Z+1 in a lattice of atoms Z. Very good experimental and theoretical agreement was found for a range

of elements using this scheme.

The model of equivalent cores was later extended^{6.34, 6.35} to include an explanation of the shifts observed in dilute alloys. Now, additional terms must be included to account for the heat of solution of atom A and A^+ ($\equiv A+1$) in matrix AB,

$$\Delta E_{\text{Calc}} = E(A; AB) + E(A+1; A) - E(A+1; AB) \quad (6.1)$$

where $E(A; AB)$ is the energy of solution of atom A in matrix AB, $E(A+1; A)$ represents the heat of solution of the core ionised atom A^+ in A and $E(A+1; AB)$ is the energy of solution of the core ionised atom A^+ in matrix AB. For the case of CoTi, the binding energy shifts between the elemental metals and the alloy are,

$$\begin{aligned} \Delta E_{\text{Calc Ti}} &= E(\text{Ti}; \text{CoTi}) + E(\text{V}; \text{Ti}) - E(\text{V}; \text{CoTi}) \\ \Delta E_{\text{Calc Co}} &= E(\text{Co}; \text{CoTi}) + E(\text{Ni}; \text{Co}) - E(\text{Ni}; \text{CoTi}) \end{aligned} \quad (6.2)$$

The first term represents changes in the initial state bonding of A whilst the second and third represent changes associated with the final state A^+ configuration in A and AB. The last term involves a ternary (A, A+1, B) compound and so is difficult to calculate except when $Z(B) = Z(A+1)$ ie. adjacent atoms in the periodic table. The second term in equations 6.1 and 6.2 are usually small ($<200\text{meV}$), and if the two metals A and B have different metallurgical properties (as in Co and Ti), the balance of the first and third term determine the magnitude of the core shift.

6.10 HREEL Spectra of CoTi Oxidation

Since XPS has characterised the irreducible surface oxide on both annealed and unannealed CoTi surfaces as TiO-like, and has shown that Co remains in the metallic state, it is possible to associate the 65meV loss feature seen on the annealed surface in HREELS as due to TiO. Indeed, a comparison with the earlier spectra of the initial stages of oxidation of Ti for exposures of $<1\text{L}$ (see chapter 4), shows an identical loss peak is seen on Ti(0001). There it was concluded, with the aid of literature, that this feature is due to a simple Ti-O stretch with O at a three-fold hollow site and can be

linked to the growth of Ti^{2+} oxide by XPS. Since a very similar loss energy is observed for the irreducible O vibration at the CoTi surface, it can be concluded that some major surface rearrangement has occurred to provide a Ti three-fold hollow site, but since no LEED patterns were obtained a more detailed structural model cannot be justified. The CoTi(110) would be expected to have four-fold and not three-fold symmetry as in Ti(0001).

It is also observed that the intensity of the loss feature is very much greater than the loss intensity of the equivalent feature seen in Ti(0001) oxidation. Such a large concentration of TiO is never seen on the Ti single crystal surface without the presence of other suboxides and HREELS showed that it is only for exposures of $<1\text{L}$ that this type of loss spectrum can be seen on Ti(0001). It is obvious that the HREELS beam is probing a CoTi surface with a considerable oxygen concentration.

6.11 The Oxidation of Related Materials

It is interesting to compare the oxidation behaviour of CoTi with the related intermetallic alloys FeTi and FeTi_2 as similarities have already been found in sputtering behaviour. Most work on these materials has concentrated on model activation cycles in which the alloy is heated in a small partial pressure of oxygen. However, some basic surface characterisation has been performed.

Similar investigations on FeTi by Polak *et al*, has produced several useful papers^{6.36, 6.37, 6.38}. A sputtered FeTi surface (not annealed) was allowed to reside in UHV whilst the growth of oxide as a direct result of residual gas interaction was monitored with time in vacuum. Reaction occurred between residual H_2O (inferred) and Ti atoms, the Fe remaining unchanged. After 20 hours in UHV (approximate exposure of $1\text{L H}_2\text{O}$), peaks assignable to Ti^{2+} , and later Ti^{3+} , were visible in the Ti core level spectrum. No surface segregation of Ti atoms was noted. Such a study should be viewed with some caution since exposure of any surface to residual vacuum is very uncontrolled both in the dose and, more importantly, reacting species.

The oxidation behaviour of three potential hydrogen storage materials, FeTi, NiTi and the oxygen stabilised phase $\text{Fe}_2\text{Ti}_4\text{O}$, have been

compared^{6.39} using AES. In all three instances, oxygen reacted preferentially with the Ti component, the Fe remaining unoxidised at room temperature. The authors suggest that TiO₂ is the major product, AES features due to TiO₂ being detectable at 1L exposure in Fe₂Ti₄O and 2L exposure in FeTi and NiTi. In these instances, oxidation induced Ti surface segregation was noted.

The interaction of FeTi with hydrogen has been studied by Sicking and Jungblut^{6.40}. After H₂ dosing a FeTi sample at 800°C in UHV, very pronounced Ti surface segregation occurred, with Fe absent from about 100 atomic layers. Below this region, no Fe enrichment above bulk values was found. Since hydrogen is the major residual gas in most UHV systems, heating of such intermetallics alone may cause significant Ti diffusion. The synergistic effect of O₂ in the presence of H₂ is unclear. Although the role of residual hydrogen cannot be assessed in the work presented here, Sicking and Jungblut comment that the tendency of bulk dissolved O to segregate to the surface is increased in the presence of gas phase hydrogen.

Other work presents a much more confused picture with contradictory reports of oxidation products. Zuchner and Kirch^{6.41} and Schlapbach^{6.42} have reviewed much of the earlier work. Air exposed FeTi surfaces show evidence for oxidation of both Fe and Ti. It will be recalled that the CoTi surface as-presented (after air exposure) showed both Ti and Co oxides in contrast to exposure to O₂ only in the UHV chamber, which showed oxidation of Ti only. It will also be recalled that different oxidation products result on elemental Co if exposed to air or oxygen (chapter 5). However, using AES they found that heating the air exposed samples in poor vacuum conditions, where there is a significant oxygen partial pressure, led to preferential oxidation of Ti, with precipitation of metallic Fe on the surface of the sample.

Surface Fe islands may also be implied in the Auger and SIMS depth profiles of Zuchner *et al*^{6.43}. Schlapbach *et al*^{6.44} found that activated FeTi surfaces prepared by ion bombardment, followed by heating at 400°C in 10⁻⁵bar oxygen had a Fe deficient Ti-oxide surface layer with an iron rich/titanium deficient subsurface layer. Selected area transmission electron microscopy of an activated FeTi surface showed diffraction spots due to

TiO₂, TiO and Fe₃O₄, although spots due to metallic Fe were not identified^{6.45}.

An XPS study of room temperature oxidation of vacuum cleaved FeTi and Fe₂Ti₄O_{0.6}^{6.46} by exposure to *air* showed initial oxygen exposure leads to formation of TiO. However, after 1000L air exposure there is clear evidence for oxidation of Ti to Ti⁴⁺ and of Fe to Fe³⁺ and Fe²⁺. Exposure to O₂ led to an increased Ti:Fe XPS intensity ratio in the case of the oxygen stabilised phase but not in the case of FeTi. Other authors^{6.47} noted a decrease in Ti segregation once an oxygen free AES spectrum was obtained and a strong LEED pattern established. Hence, it appears that the Ti segregation effects may be linked to O segregation.

Values for the binding energy shift of the Ti:2p_{3/2} peak of FeTi relative to Ti metal vary between +0.7eV^{6.48} and +0.3eV^{6.46}. Similar effects have been noted in Fe:2p XPS spectra of FeTi^{6.46} where there was an increase in the Fe:2p binding energy relative Fe metal (Fe metal 2p_{3/2}=706.9eV, Fe in FeTi 2p_{3/2}=707.1eV).

6.12 Conclusions

The oxidation of annealed and unannealed CoTi surfaces followed by XPS has shown,

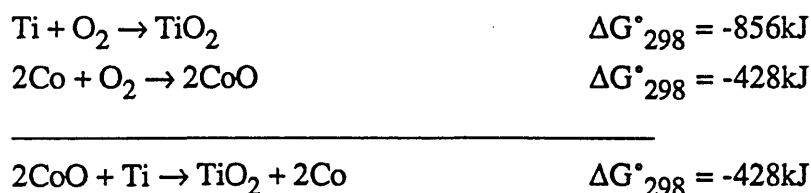
- (i) oxidation of the Ti component only occurs with exposures up to 7500L O₂ at room temperature. No Co oxides are formed up to these exposures, but surfaces exposed to air for long periods show outer layers of Co oxides/hydroxides, TiO₂ and Ti metal.
- (ii) The oxidised CoTi surface is inhomogeneous and is composed of TiO, Ti₂O₃ and TiO₂-like oxides. TiO forms at low exposures, but the dominant oxide becomes TiO₂ at moderate exposures. The series of oxides formed parallels the behaviour of Ti(0001) metal.
- (iii) The unannealed surfaces of CoTi show a greater reactivity toward oxygen than the annealed surfaces although the same sequence of oxidation products are observed.

(iv) Shifts in the core level lines of Co and Ti in CoTi are inconsistent with a charge transfer mechanism as has been proposed previously for FeTi.

(v) Oxygen induced Ti segregation is found for the annealed and unannealed surfaces. Both O and Ti diffuse to the alloy surface during the course of surface preparation.

HREELS shows that the irreducible oxygen content of the surface exhibits a single loss peak at 65meV which is much more intense than the 65meV peak seen for very small doses of O₂ on the Ti(0001) surface. Exposure of the CoTi surface to O₂ at room temperature results in the growth of structure at 90-95meV in a similar manner to Ti. At no time was it possible to observe losses assignable to metal-H vibrations

Total inhibition of Co oxidation in CoTi is perhaps at first glance the most striking result to emerge from the present study since the reactions of Fe, Co and Ti with O are all strongly exothermic (ΔH_f TiO = -520kJmol⁻¹, TiO₂ = -945kJmol⁻¹, CoO = -239kJmol⁻¹, FeO = -270kJmol⁻¹)^{6.49}. The submersion of Co beneath the Ti oxide overlayer may provide a simple structural mechanism for passivation of the Co, but it is more probable that the explanation may lie in thermodynamic arguments. TiO₂ has a greater free energy of formation than CoO ($\Delta G^\circ_{298}(\text{CoO}) = -214.2\text{kJmol}^{-1}$, $(\text{TiO}_2) = -856\text{kJmol}^{-1}$)^{6.50} and so is (thermodynamically) the more stable oxide. Hence, metallic Ti would be expected to reduce CoO according to,



Therefore, the formation of CoO at the CoTi surface is thermodynamically unfavourable as long as some metallic Ti remains unoxidised.

6.13 References

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7. Further Studies of the Co-Ti Alloy System: Co_3Ti and CoTi_2

7.1 Surface Preparation of Co_3Ti and CoTi_2

The Co_3Ti and CoTi_2 alloy samples were prepared by arc-melting the appropriate masses of the constituent components. The sample slices ($\approx 7\text{-}9 \times 1\text{mm}$) obtained from the slitting machine were polished down to $1/4\mu$ using diamond paste and a water based lubricant. The specimens were rinsed in propan-2-ol and distilled water in an ultrasound bath, mounted on sample stubs and placed into the (previously baked) ESCALAB preparation chamber where they were annealed for 8hrs each at $\approx 600^\circ\text{C}$ to improve phase homogeneity as described in detail in chapter 3. The samples were removed from the chamber after annealing to facilitate XRD measurement and were left in a laboratory atmosphere for several weeks before being inserted into the vacuum chamber again. These surfaces were analysed by Mg $\text{K}\alpha$ XPS in the VG ESCALAB.

The Ti:2p regions of the two air exposed alloys, shown in figure 7.1, essentially exhibit the same features as that of the CoTi alloy after a period of air exposure which is also shown in the figure for comparison. Two pairs of overlapping spin-orbit doublets due to metallic Ti and Ti (IV) oxide can be seen. Similarly, features in the Co:2p_{3/2} region in figure 7.2, show a narrow peak at 778.3eV together with structure at 781/782eV and 787eV. The higher binding energy features are associated with Co oxides and/or hydroxide phases as discussed in chapter 6. The proportion of *metallic* Co (0) observed at the surface roughly corresponds with the concentration of Co in the bulk. It is interesting to note that the Co intensity is immediately visible in Co_3Ti and CoTi_2 without any sputtering, unlike the polished CoTi sample, but this may be a reflection of the phase annealing performed.

Both surfaces were then sputtered in the ESCALAB preparation chamber until contamination levels reached minimum values as judged by Mg XPS. After a period of a few hours sputtering by 2-3keV Ar^+ ions, the surfaces were free of any measurable C, but O could not be eliminated entirely from either surface. It will be recalled that sample oxygen content was estimated from the pre- and post-melt masses and was estimated at 710 ppm for Co_3Ti and 520 ppm for CoTi_2 . The samples were annealed then at

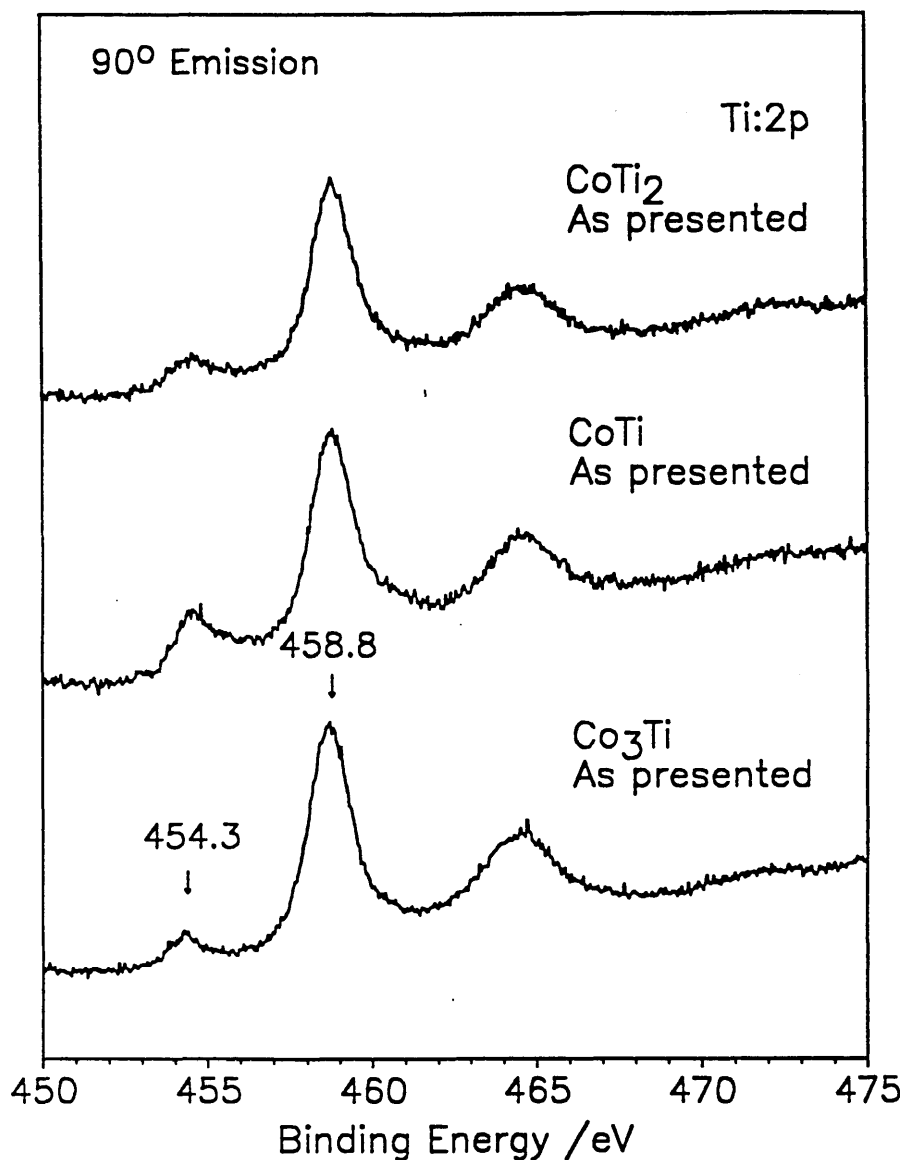


Figure 7.1: Mg $K\alpha_{1,2}$ XPS of the Ti:2p region of the three alloys CoTi₂, Co₃Ti and CoTi as entered the ESCALAB vacuum system. The CoTi surface had previously been cleaned to low O and C levels by sputtering and then exposed to air for several weeks. The CoTi₂ and Co₃Ti surfaces had been annealed in vacuum at 550-650°C for 8hrs after fabrication and then exposed to air for several weeks. All three surfaces show features attributable to minor Ti (0) and major Ti (IV) oxide concentrations.

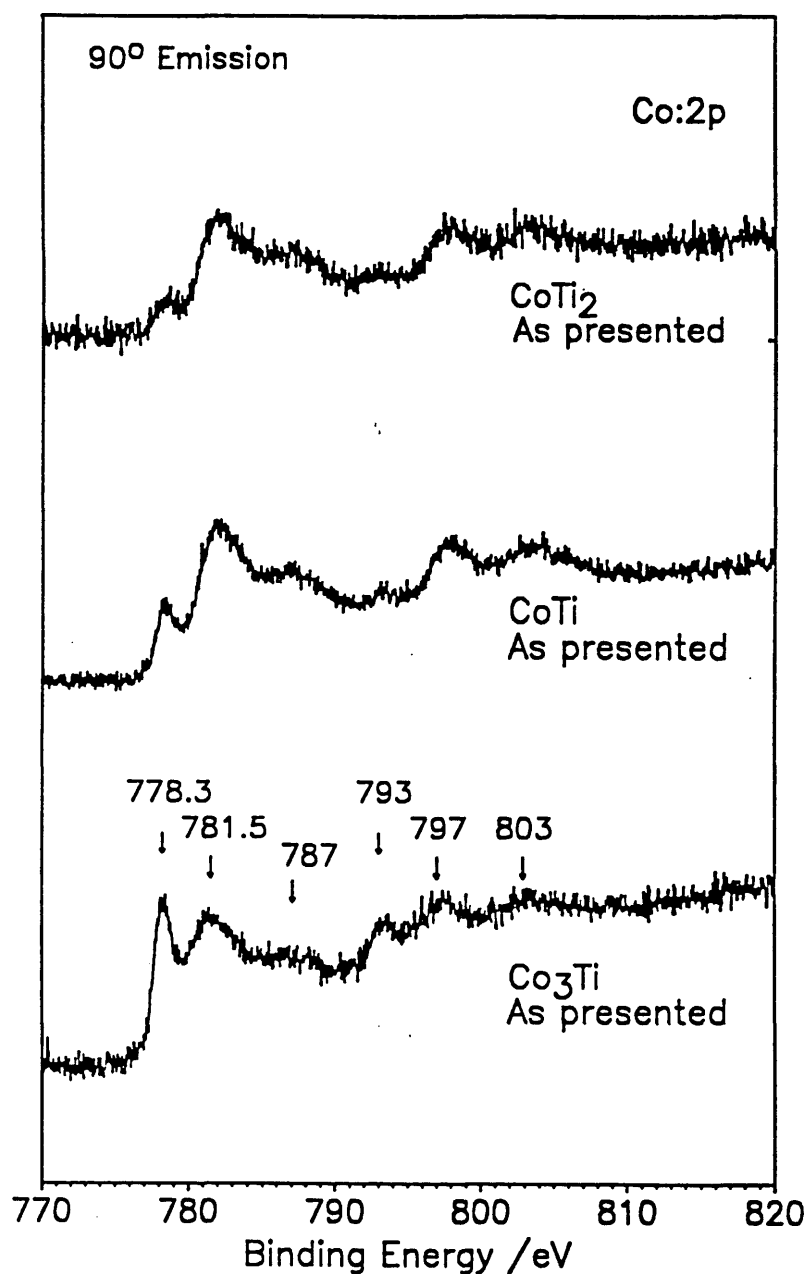


Figure 7.2: Mg $K\alpha_{1,2}$ XPS of the Co:2p region of the three alloys CoTi₂, Co₃Ti and CoTi as entered the ESCALAB vacuum system. Sample treatment prior to these spectra described in the caption for figure 7.1. The three surfaces show features attributable to Co (0) at ≈ 778 eV ($2p_{3/2}$) and ≈ 793 eV ($2p_{1/2}$). Other features are due to Co oxides/hydroxides.

550-650°C until the Co:Ti ratio was close to the nominal value as measured by XPS.

7.2 The Oxidation of Co_3Ti

The annealed Co_3Ti surface gave a XPS intensity ratio of Co:Ti:O:C = 6.2 : 1 : 0.13 : ≈ 0 , which corresponds to a stoichiometry of $\text{Co}_{2.92}\text{TiO}_{0.31}$. The $2p_{3/2}$ peak maximum of annealed Co_3Ti shown in figure 7.3, occurs at 454.7eV binding energy consistent with the presence of both Ti and TiO species. Exposure to only 7.5L O_2 produces very dramatic change at the surface as evidenced by the growth of a distinct shoulder at the high binding energy side of the original Ti: $2p_{3/2}$ peak. After exposure to 75L O_2 , a feature at $\approx 459\text{eV}$ becomes obvious and it is this feature that dominates the Ti: $2p$ region after 7500L and 15000L O_2 .

In contrast, no changes are seen in the Co: $2p$ spectra (not shown) except for some slight peak attenuation with oxygen exposure. Maximum $2p_{3/2}$ intensity occurs at 778.2eV binding energy, identical to that of Co metal measured in chapter 6 (within experimental error). This will be discussed later.

Figure 7.4 shows the results of subtracting the Ti: $2p$ spectrum of annealed Co_3Ti from the oxygen exposed Ti: $2p$ regions as was performed for CoTi in chapter 6. Exposure to 7.5L O_2 (figure 7.4(a)) results in intensity growth throughout the region 456 $\rightarrow$ 459eV corresponding to an increase in Ti (III) and (IV) concentration. By 75L O_2 exposure, intensity growth has concentrated around 459eV indicating dominance of TiO_2 . The proportion of Ti (IV) then increases with exposure up to 15000L. Maximum loss in intensity occurs at roughly constant binding energy throughout at 455.0eV, indicating the Ti (0) binding energy in Co_3Ti at this value. This is shifted some +1.2eV with respect to Ti metal and +0.5eV with respect to CoTi.

7.3 The Oxidation of CoTi_2

Turning to the CoTi_2 surface, the initial XPS intensity ratio of Co:Ti:O:C = 1 : 1 : 0.05 : ≈ 0 is consistent with a stoichiometry of

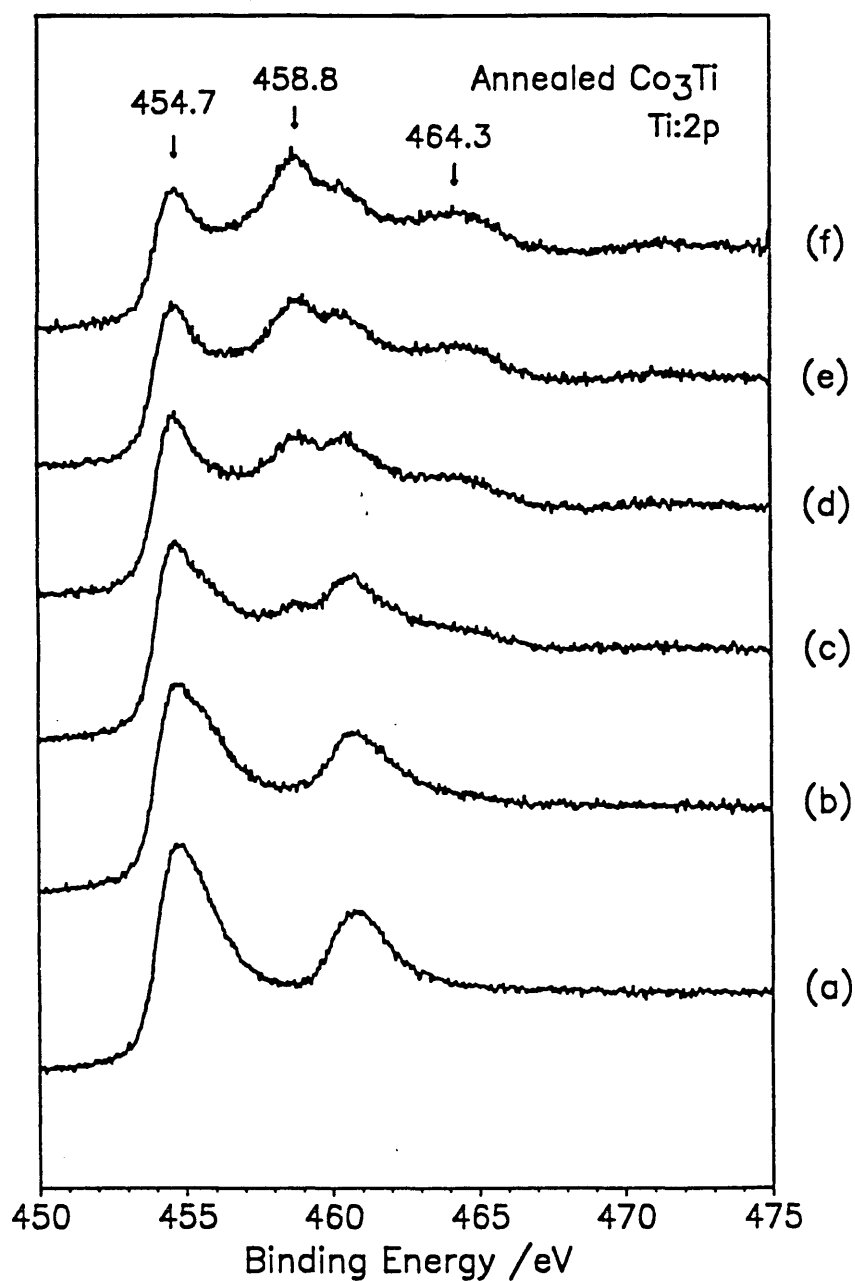


Figure 7.3: Mg $K\alpha_{1,2}$ XPS of the Ti:2p region of annealed Co_3Ti with O_2 exposure (a) 0L (b) 7.5L (c) 75L (d) 750L (e) 7500L (f) 15000L at room temperature and measured at normal emission. Note the appearance of features due to TiO_2 .

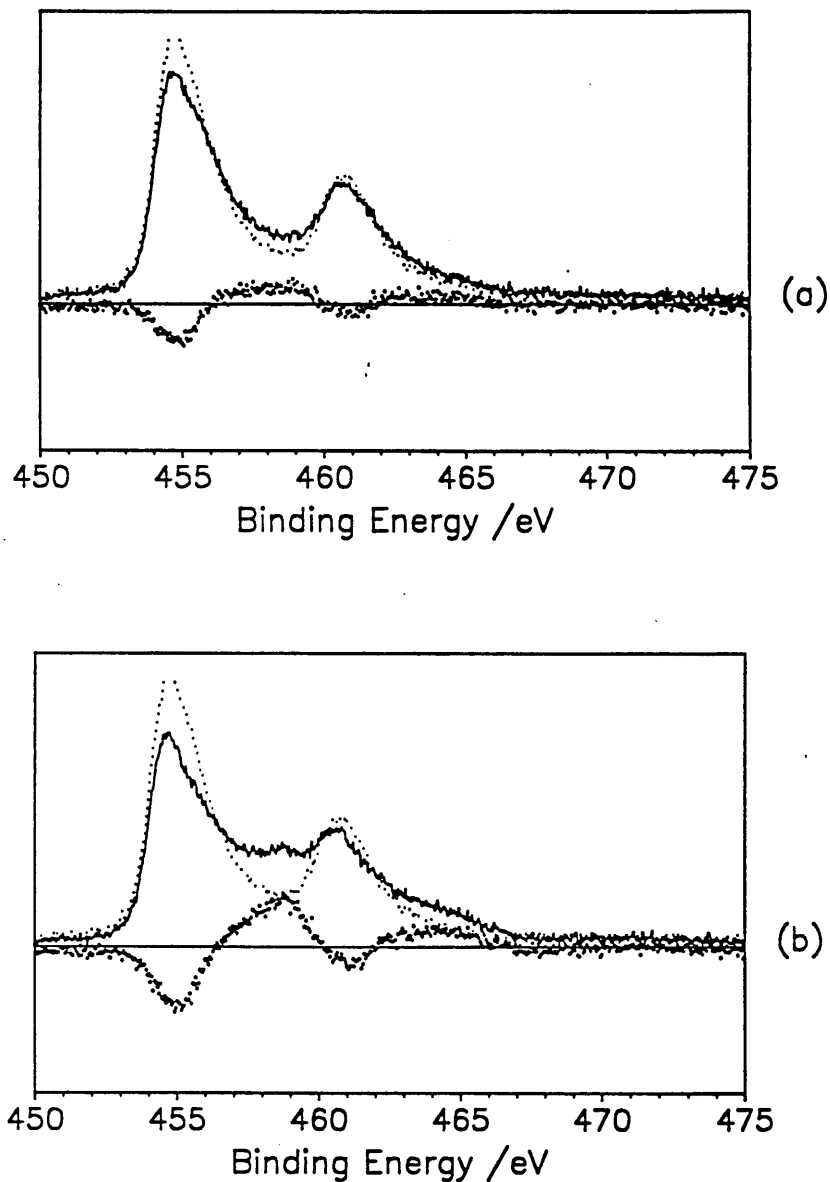


Figure 7.4: Mg K α XPS spectra of the Ti:2p region of Co₃Ti after exposure to O₂ (a) 7.5L (b) 75L at room temperature. In each case, the light dots represent the annealed Ti:2p region, the solid line the O₂ exposed Ti:2p region and the heavy dots the results of subtracting the oxidised spectrum from the clean spectrum. Spectra were measured at normal emission and a suitable inelastic background has been subtracted from each.

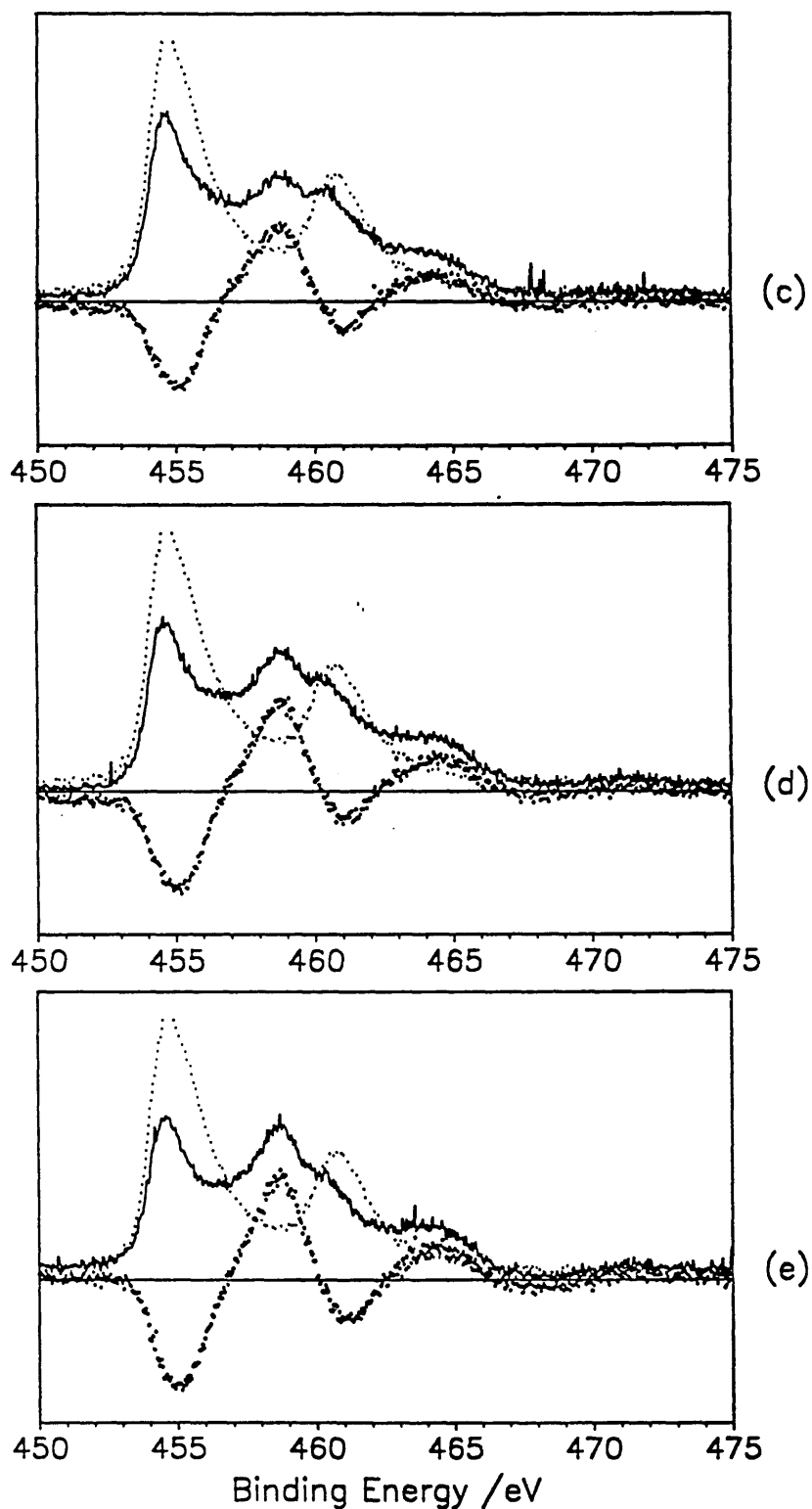


Figure 7.4 (continued): Mg $K\alpha$ XPS spectra of the Ti:2p region of Co_3Ti after exposure to O_2 (c) 750L (d) 7500L (e) 15000L at room temperature. In each case, the light dots represent the annealed Ti:2p region, the solid line the O_2 exposed Ti:2p region and the heavy dots the results of subtracting the oxidised spectrum from the clean spectrum.

$\text{CoTi}_{2.1}\text{O}_{0.11}$ after annealing. This represents the lowest O surface content experienced in any of the annealed alloys. It will be recalled that the estimated bulk O content of CoTi_2 was lower than Co_3Ti and this is probably reflected in the lower surface O content. Indeed, Ti:2p XPS of annealed CoTi_2 , given in figure 7.5, shows that the lineshape of the alloy is only slightly broader than the that of clean Ti metal correlating with only a small Ti (II) surface concentration.

The $2p_{3/2}$ peak is located at 454.4eV and the $2p_{1/2}$ at 460.4eV, some 0.6eV higher binding energy than that of Ti metal for the reasons discussed in chapter 6.

In this instance, the appearance of features attributable to Ti (IV) oxide formation occurs much less rapidly with oxygen exposure than for the other annealed surfaces, but some structure due to TiO_2 is visible in the highest exposure spectra. Some shift to higher binding energy is observed in the highest exposure, and a slight broadening of the initial $2p_{3/2}$ peak is seen in the 7.5 and 75L O_2 exposures indicating that there is some increase in TiO concentration in this range. Again, in the Co:2p region of CoTi_2 (not shown), no change is observed. Some slight peak intensity decrease relative to the inelastic background is apparent. The Co: $2p_{3/2}$ peak is located at $\approx 778.3\text{eV}$ binding energy.

Figure 7.6 shows the difference data of the Ti:2p region of CoTi_2 taken for the various oxygen exposures minus the spectrum of the annealed surface. Changes are broadly in line with those of all the other Co-Ti alloys; a loss in intensity corresponding to Ti (0) together with eventual dominance by TiO_2 with substantial concentrations of TiO and Ti_2O_3 . In the case of CoTi_2 , the position of maximum loss in intensity (corresponding to Ti (0)), occurs at 454.2eV.

When taken in conjunction with the inferred Ti (0): $2p_{3/2}$ peak position of the other alloys, indicates that the magnitude of the Ti (0) peak shift decreases as the Ti concentration in the alloy is increased. The binding energy of the Ti: $2p_{3/2}$ peak in each of the alloys inferred from the difference data, is collected in table 7.2.

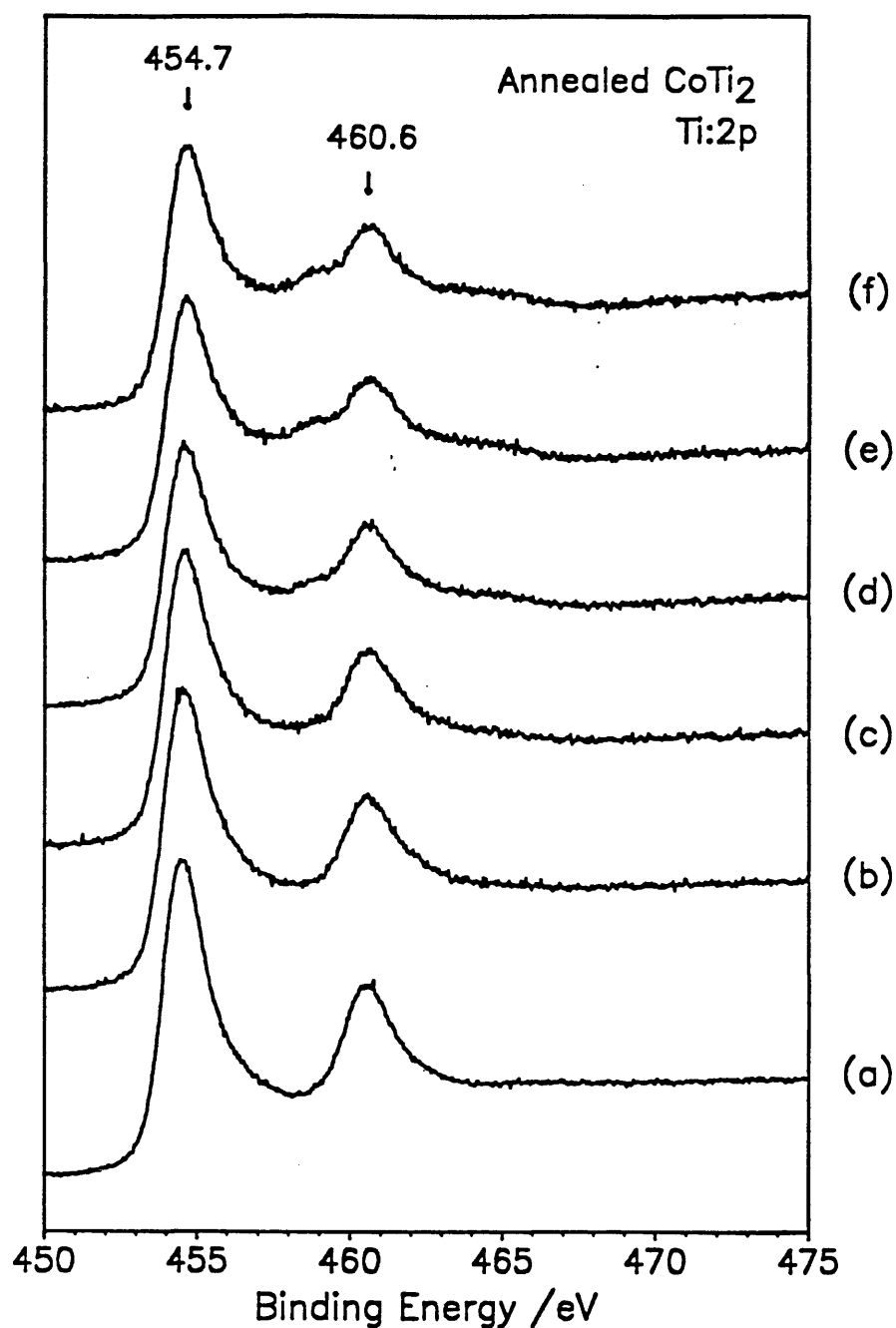


Figure 7.5: Mg $K\alpha_{1,2}$ XPS of the Ti:2p region of annealed CoTi₂ with O₂ exposure (a) 0L (b) 7.5L (c) 75L (d) 750L (e) 7500L (f) 15000L at room temperature and measured at normal emission. Note the narrow initial lineshape of both 2p peaks and the appearance of relatively weak features due to TiO₂.

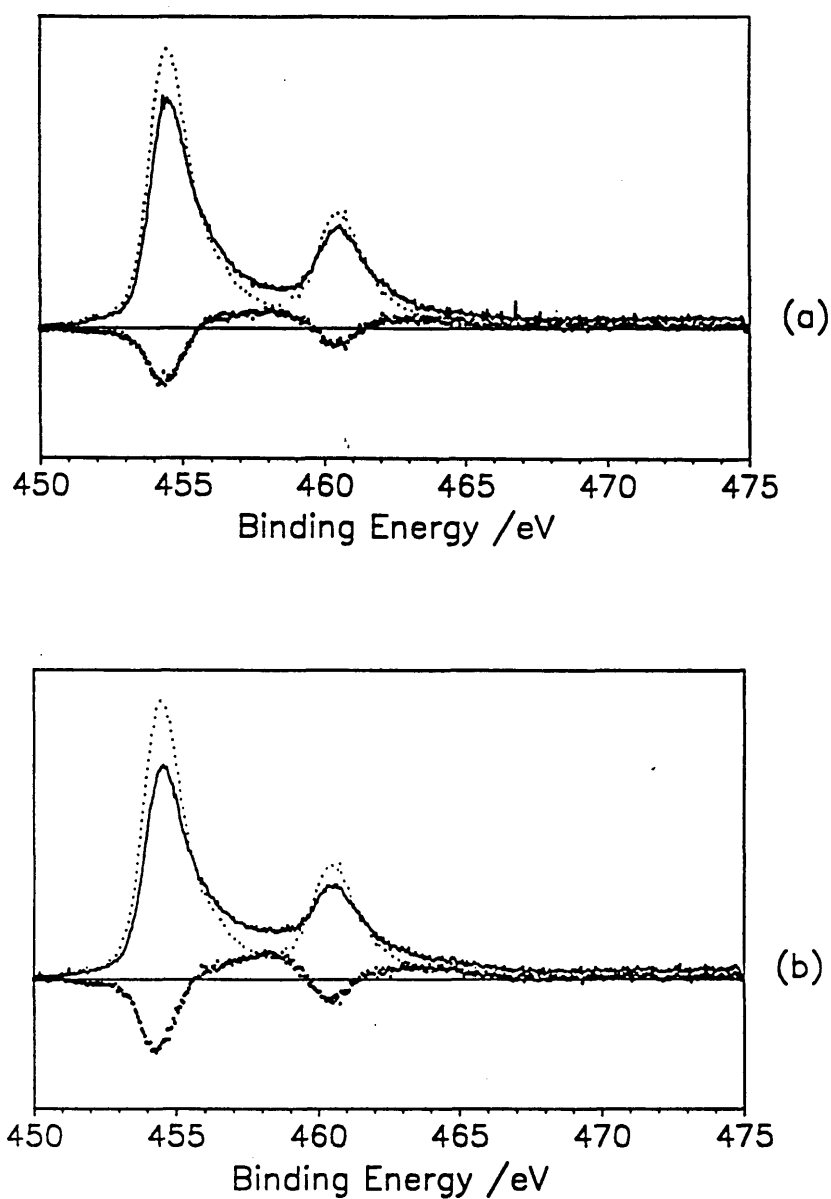


Figure 7.6: Mg K α XPS spectra of the Ti:2p region of CoTi₂ after exposure to O₂ (a) 7.5L (b) 75L at room temperature. In each case, the light dots represent the annealed Ti:2p region, the solid line the O₂ exposed Ti:2p region and the heavy dots the results of subtracting the oxidised spectrum from the clean spectrum. Spectra were measured at normal emission and a suitable inelastic background has been subtracted from each.

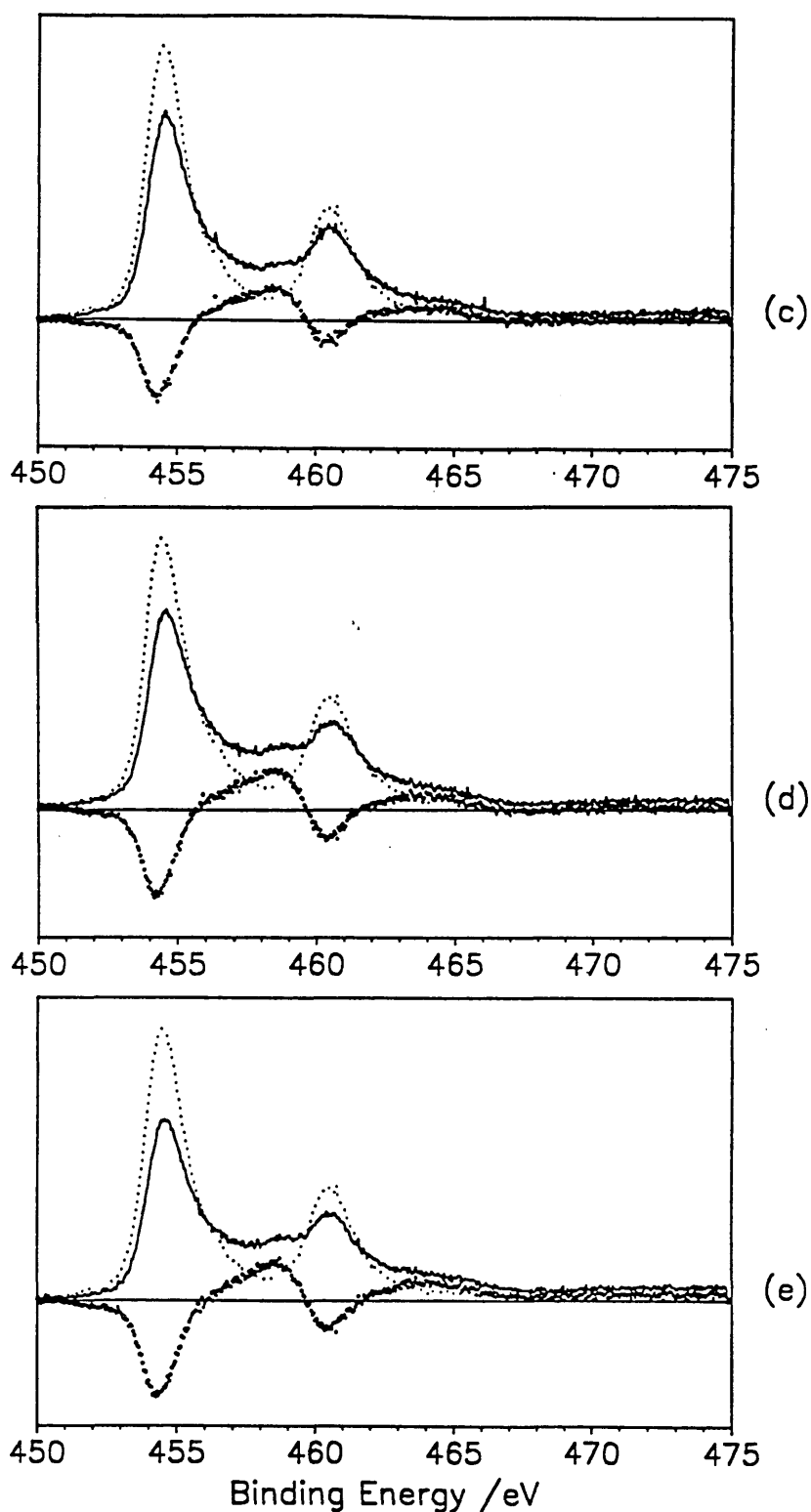


Figure 7.6 (continued): Mg K α XPS spectra of the Ti:2p region of CoTi₂ after exposure to O₂ (c) 750L (d) 7500L (e) 15000L at room temperature. In each case, the light dots represent the annealed Ti:2p region, the solid line the O₂ exposed Ti:2p region and the heavy dots the results of subtracting the oxidised spectrum from the clean spectrum.

Table 7.1: Binding energy of $\text{Ti}^{0:2p_{3/2}}$ in Ti and Co-Ti alloys

	Binding Energy /eV
Ti metal	453.8
CoTi_2	454.2
CoTi	454.5
Co_3Ti	455.0

The changes in surface composition in both CoTi_2 and Co_3Ti induced by oxygen exposure are shown in figure 7.7. The figure shows that a decrease in the Co:Ti ratio occurs in both cases upon oxidation implying Ti segregation. The Co:Ti stoichiometry (from corrected XPS intensities) for Co_3Ti falls from 2.92 at the annealed surface to 2.67 after 15000L O_2 . The Co:Ti stoichiometry for CoTi_2 falls from 0.46 to 0.42 after 15000L O_2 . The increase in the O:Ti ratio is greatest in the case of Co_3Ti and is comparable with the behaviour of the sputtered CoTi surface. The rate of O:1s increase on the annealed CoTi_2 is much less rapid than for either CoTi or Co_3Ti .

7.4 Valence Band of Co-Ti Alloys

The valence bands of the annealed alloys Co_3Ti , CoTi and CoTi_2 together with valence bands for clean Ti and Co metals, are shown in figure 7.8. The spectra are arranged so that overall Co concentration decreases going from bottom to top. The spectra show the Co-Ti:3d band at just below E_F , contamination O:2p states at $\approx 6\text{eV}$ and the Ti:3p states at $\approx 33\text{eV}$ binding energy. Mixed Ti:3p x-ray satellite structure and O:2s states are seen at 21-25eV binding energy. The spectra have been normalised so that the Ti:3p intensity corresponds with that expected from the bulk composition.

It is obvious from the figure that the maximum d band intensity decreases upon going from $\text{Co} \rightarrow \text{Co}_3\text{Ti} \rightarrow \text{CoTi} \rightarrow \text{CoTi}_2 \rightarrow \text{Ti}$. This drop is due in part to changes in the relative 3d cross sections per d electron for each atom ($\sigma_{\text{Ti:3d}}=0.008$, $\sigma_{\text{Co:3d}}=0.043^{7.1}$), and in part to the higher d band occupancy of Co compared with Ti. As a result, the d band intensity seen in the valence band spectra of the three Co-Ti alloys will be dominated by the Co:3d states. The average electron count per metal atom (3d+4s) of Co_3Ti , CoTi and CoTi_2 is 7.75, 6.5 and 5.6 respectively.

If the valence region is expanded and normalised so that the maximum valence band height is constant, as shown in figure 7.9, subtle changes in the region around E_F can be observed. In particular, the position of the d band maximum is found to shift away from the Fermi edge as Co is diluted in the series $\text{Co} \rightarrow \text{Co}_3\text{Ti} \rightarrow \text{CoTi} \rightarrow \text{CoTi}_2$. The d band maximum is at 0.7eV in Co metal but has shifted to 1.4eV binding energy in CoTi_2 . Simultaneously, there is a reduction in the DOS at the Fermi level relative to

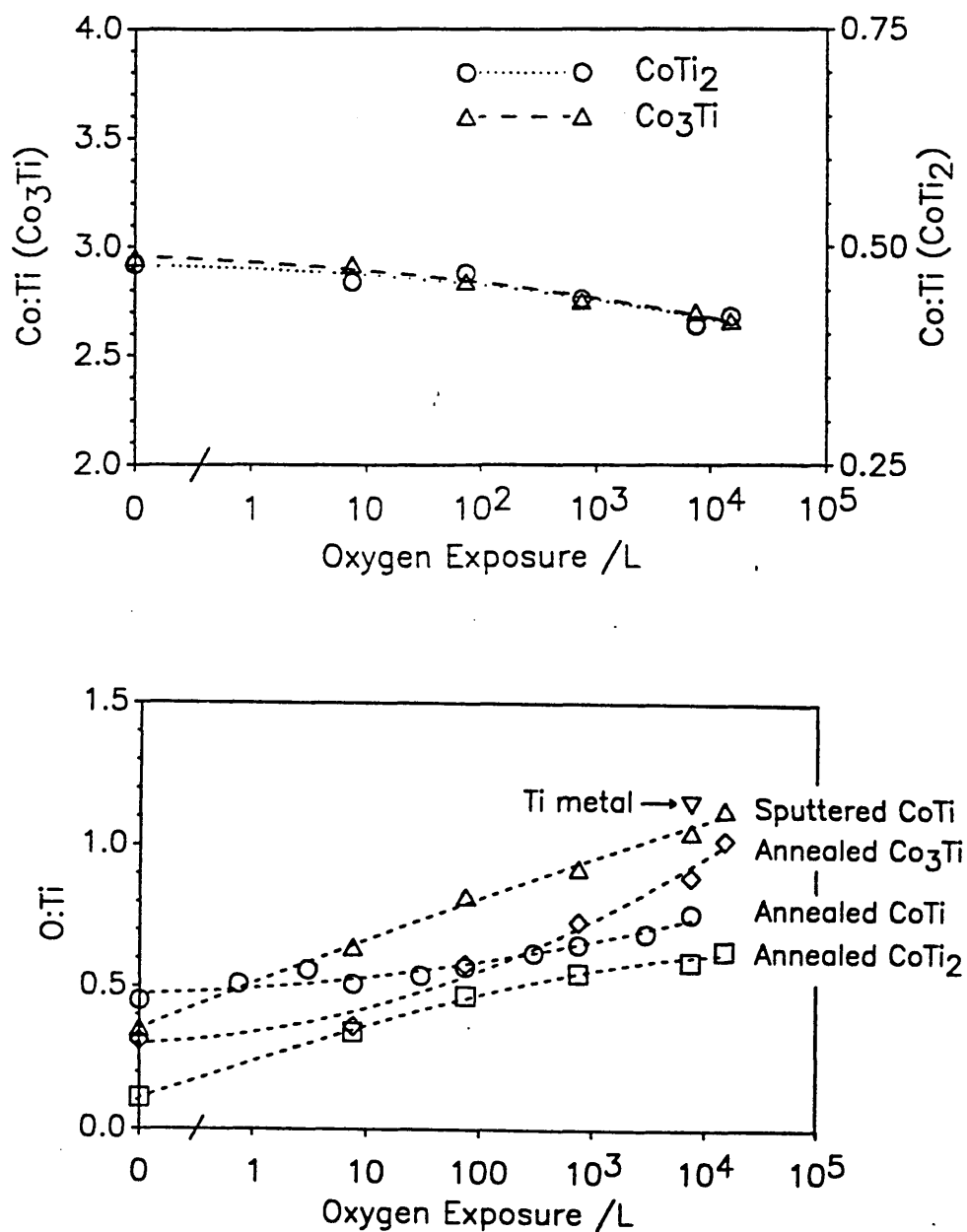


Figure 7.7: Top panel: Changes in the Co:Ti ratio for Co₃Ti and CoTi₂ induced by exposure to O₂ at room temperature. The left Y scale refers to Co₃Ti and the right Y scale CoTi₂. In both cases, Ti segregation occurs. Bottom panel: Increase in the O:Ti ratio as oxidation proceeds for Co₃Ti and CoTi₂. Data for sputtered and annealed CoTi is also included. The ratio increases most quickly for the alloy with the lowest Ti concentration.

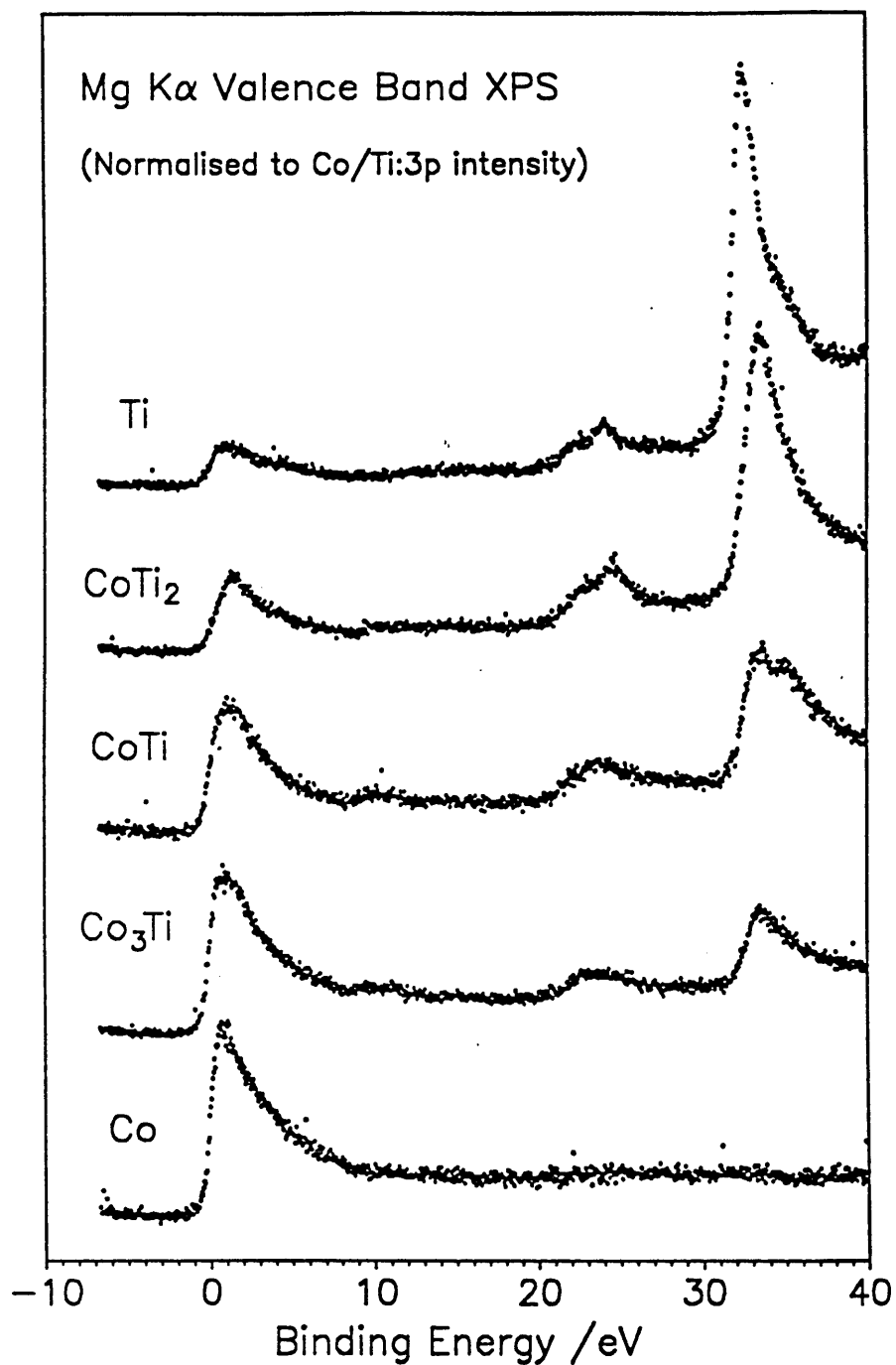


Figure 7.8: Mg K α excited ($h\nu=1254\text{eV}$) valence band spectra for Ti metal, CoTi₂, CoTi, Co₃Ti and Co metal. Spectra have not been stripped of K $\alpha_{3,4}$ contributions and are normalised to the Co/Ti:3p intensity expected from bulk concentrations. The Fermi level is fixed at $1/2$ d band intensity for Co metal.

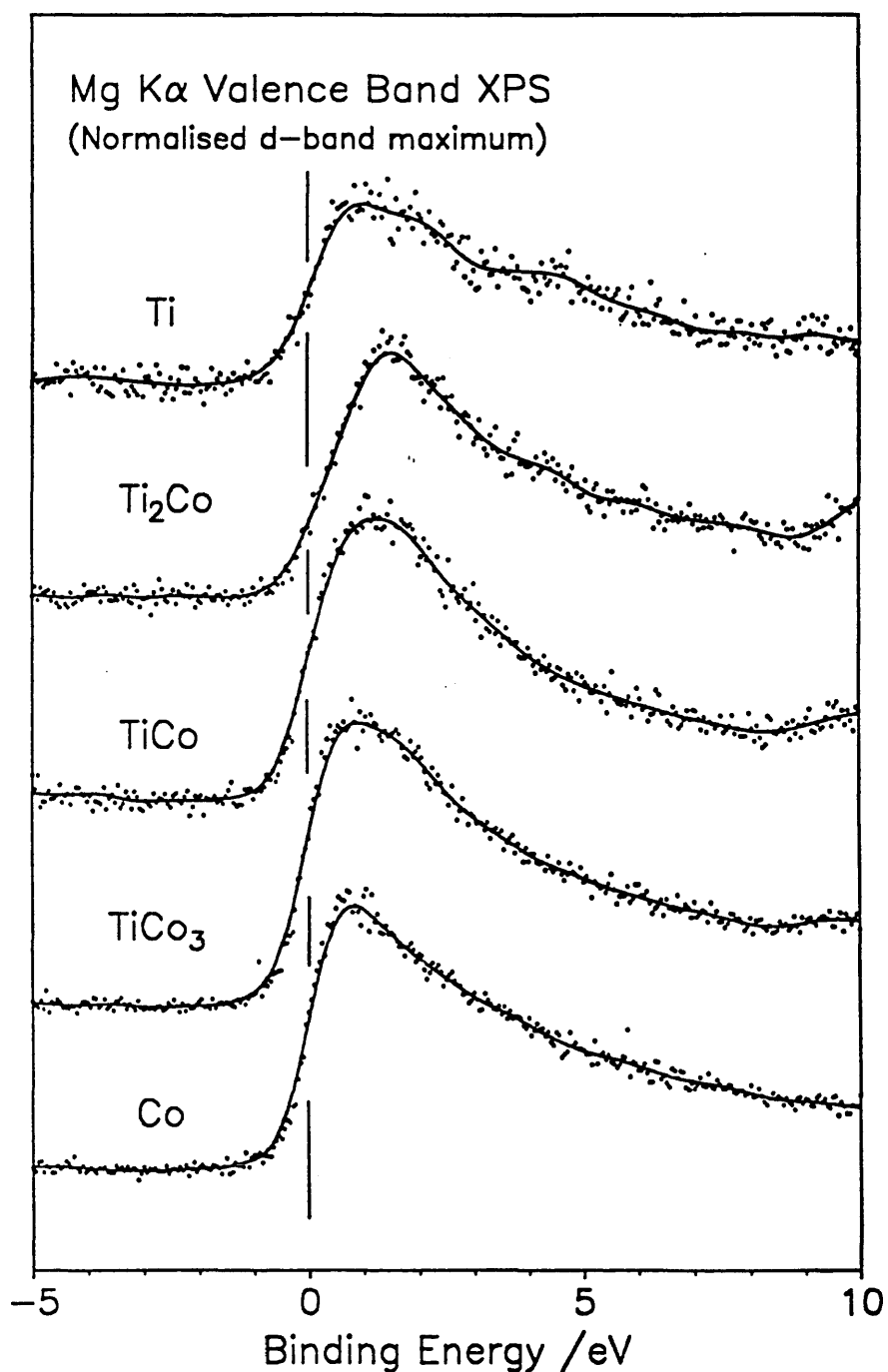


Figure 7.9: Detail around Fermi level from figure 7.8 of the d band intensity associated with Ti metal, CoTi₂, CoTi, Co₃Ti and Co metal. In this case, the spectra have been normalised to maximum d band intensity. Note the shift of d band maximum and decrease in intensity at E_F with Co dilution in the alloys. No K $\alpha_{3,4}$ removal.

the maximum d band height from approximately 0.5 in Co (defined) to 0.3 in CoTi_2 , as shown in figure 7.10.

These observed trends suggest that the d states closest to E_F are Co-like in character. As the Co alloy component is reduced, so the dominance of Co d states is reduced resulting in an overall fall in the d band emission, a decrease in DOS at E_F , and a shift of maximum emission intensity to higher binding energy. Calculations of the partial DOS of CoTi (with FeTi and NiTi) have been made^{7.2, 7.3, 7.4} and a comparison between the measured XPS valence spectra given above and these calculations is in rather good qualitative agreement. Calculations by Eibler *et al*^{7.3} give the partial 3d DOS for Co and Ti in CoTi around the Fermi level. The calculated DOS are reproduced in figure 7.11. Maximum Co 3d DOS (of ≈ 40 states per Ryd[†] unit cell⁻¹) occurs at $\approx 1.3\text{eV}$ below E_F whilst maximum Ti 3d DOS occurs at 1.4-2.6eV below E_F and is of considerably lower density (≈ 8 states per Ryd unit cell⁻¹). The majority of the Ti 3d DOS is located above E_F (empty states) whilst the majority of the Co:3d states lie below E_F . Some (minor) s and p character (≤ 2 states per Ryd unit cell⁻¹) was also calculated to extend both above and below the Fermi level for both atoms.

The total calculated DOS for CoTi, and similarly for the related alloys FeTi and NiTi, show two major peaks: one below ('bonding band') and one above E_F ('antibonding band'). The lower is composed mostly of M:3d states (M=Fe, Co, Ni) and the upper unoccupied Ti:3d states. The addition of electrons results in the increasing occupation of antibonding states and explains the decreased stability of the CsCl structure and the increased lattice parameters^{7.5} for CoTi and NiTi with respect to FeTi. Eibler *et al* indicated 1.1 electrons in antibonding states compared with 11.2 in the bonding states for CoTi.

7.5 Co Satellite Intensities in Co-Ti Alloys

Unfortunately, the experimental resolution of the unmonochromated XPS measurements shown above and the presence of oxygen contamination, does not allow a consideration of valence band satellites in Co-Ti alloys, which are expected to be present in the Co-rich alloys and Co itself^{7.6}. However, it is possible to examine the occurrence of satellite structure in the

[†]1 Rydberg = 13.605eV

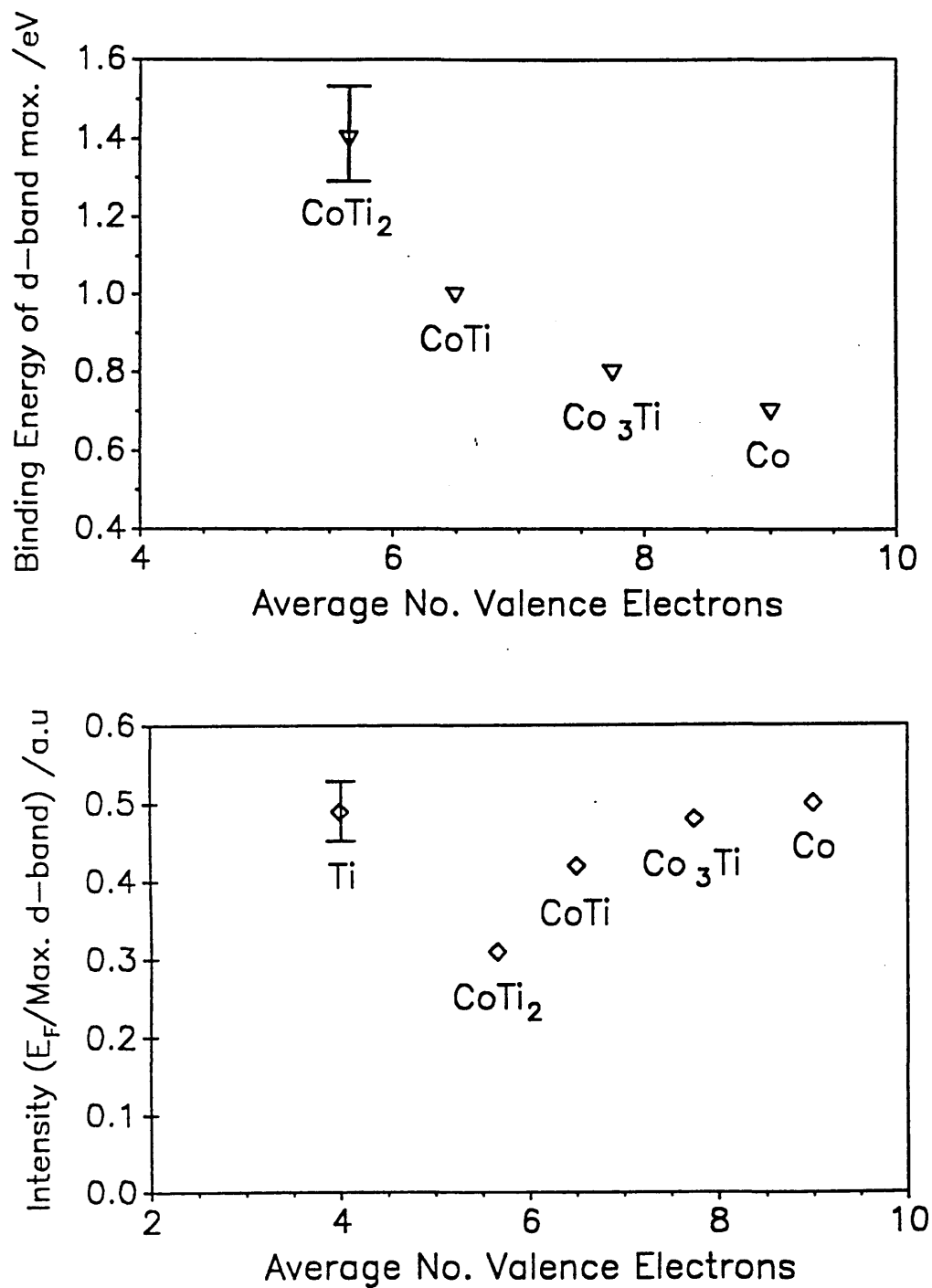


Figure 7.10: Top panel: Binding energy of d band maximum in Mg XPS valence band for Co-Ti alloys. Bottom panel: Intensity at E_F relative to maximum d band intensity for Co-Ti alloys, Co and Ti metal.

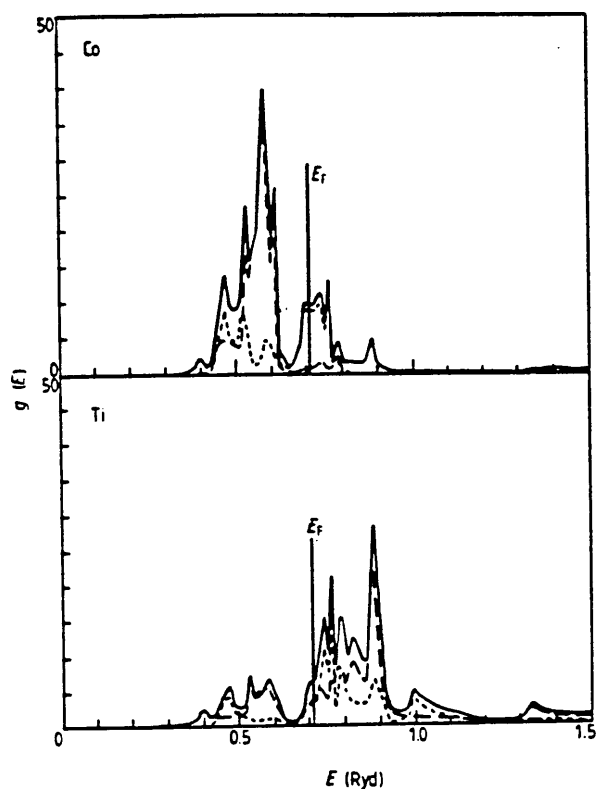


Figure 7.11: Calculated partial DOS for $\text{CoTi}^{7.3}$. The density of states $g(E)$ is in units of states $\text{Ryd}^{-1} \text{ cell}^{-1}$. E_F is at 0.71 Ryd. The local 3d DOS is shown as a solid line, and the t_{2g} and e_g components shown as a dashed and dotted line respectively

Co core levels.

Figure 7.12 shows the Co:2p_{3/2} peak for the alloys CoTi₂, CoTi and Co₃Ti and that for Co metal. A simple straight-line background has been subtracted from the spectra. In addition to the main intensity present at $\approx 778\text{eV}$, a strong satellite is visible, extending to some 9eV higher binding energy.

An examination of the Co:2p_{3/2} main intensity at $\approx 778\text{eV}$ for the three alloys and Co metal, shows that as the density of states at E_F decreases on going through the series Co $\rightarrow$ Co₃Ti $\rightarrow$ CoTi $\rightarrow$ CoTi₂, the width of the main line is observed to decrease and the peak becomes more symmetric. The creation of electron hole pairs across the Fermi edge may lead to a large number of near-degenerate final states. In a metal, this leads to the asymmetric tail to the high binding energy side of core peaks^{7,7} (so-called Doniach-Sunjic broadening). Obviously the effect is proportional to the DOS at the Fermi energy. A decrease in the Co:2p_{3/2} asymmetry, observed on going through the series Co $\rightarrow$ Co₃Ti $\rightarrow$ CoTi $\rightarrow$ CoTi₂ indicates that the probability of such core-hole excitations is reduced for Co-poor alloys, consistent with the measured decrease of states at the Fermi level measured above.

Figure 7.12 also demonstrates a decrease in Co:2p satellite intensity with Co dilution. The satellite originates as the result of many-body final state considerations as has already been mentioned in the preceding chapter. To briefly reiterate, the strong satellite intensity accompanying CoO core ionisation can be assigned to a screened and unscreened core hole final state, corresponding to the main and satellite intensity respectively. The screening electron is supplied by transfer from an O ligand.

Similarly, in a narrow band metal ($Q>W$), d states can be pulled out of the d band by core-hole Coulomb interaction upon ionisation^{7,8, 7.9}. As in metal oxides, these new localised states may be filled (screened state) or unfilled (unscreened state) but this time, the screening of the core hole is provided by valence electrons. The probability of occupation of this screening orbital depends on its coupling to the rest of the valence electrons and the degree of initial and final state occupation. As a consequence, the

spectra presented in figure 7.12, showing a decrease in satellite intensity as the Co is diluted by Ti, imply that the screening mechanism is operating more efficiently in the dilute alloys: more intensity is directed into the main (screened) intensity.

7.6 Studies of Ni Satellites in XPS: Extension to CoTi

The origin of satellite structure in Ni metal have been considered at length by many authors^{7.10, 7.11, 7.12}. The free Ni atom has an electronic configuration of $3d^8 4s^2$ but in Ni metal^{7.13}, the d electron count corresponds to $3d^{9.4}$. Therefore, the ground state can be written as a mixture of nearly degenerate $3d^9 4s^1$ and $3d^{10}$ configurations. Upon core ionisation, the $3d^{10}$ configuration is stabilised relative to $3d^9 4s^1$. The intra-atomic Coulomb interaction between two holes localised at the same Ni atom is several eV and causes the unscreened d^9 ($\equiv \underline{d}^1$) satellite structure to occur at ≈ 6 eV higher binding energy.

In a detailed series of papers by Fuggle *et al*^{7.14, 7.15, 7.16} on the valence and core levels of Ni and Pd intermetallic alloys, qualitatively very similar results were obtained for Ni alloyed with electropositive elements (early first-row transition metals). Namely, a shift in d band maximum intensity away from E_F , a fall in the overall d-band emission and a decrease in satellite intensity of core and valence peaks upon dilution of the Ni concentration. Since the probability of hole screening by the valence electrons is expected to increase as the band becomes filled, it was concluded that the Ni d band was becoming filled by alloying. Using monochromated XPS measurement of the valence bands of some 60 different alloys, it was possible to observe a recession of the Ni d band maximum as the band filled, together with a significant decrease in the bandwidth of the Ni alloys compared to Ni metal. The combination of these effects is a decreased DOS at E_F .

The band picture proposed by Fuggle *et al* based on valence and core level XPS of a great many different compounds, and shown diagrammatically in figure 7.13, suggests that when Ni is alloyed with an electropositive metal M, mixing of the Ni-M d-orbitals causes filling of the Ni d band. By alloying Ni with metals of differing electronegativities, it was

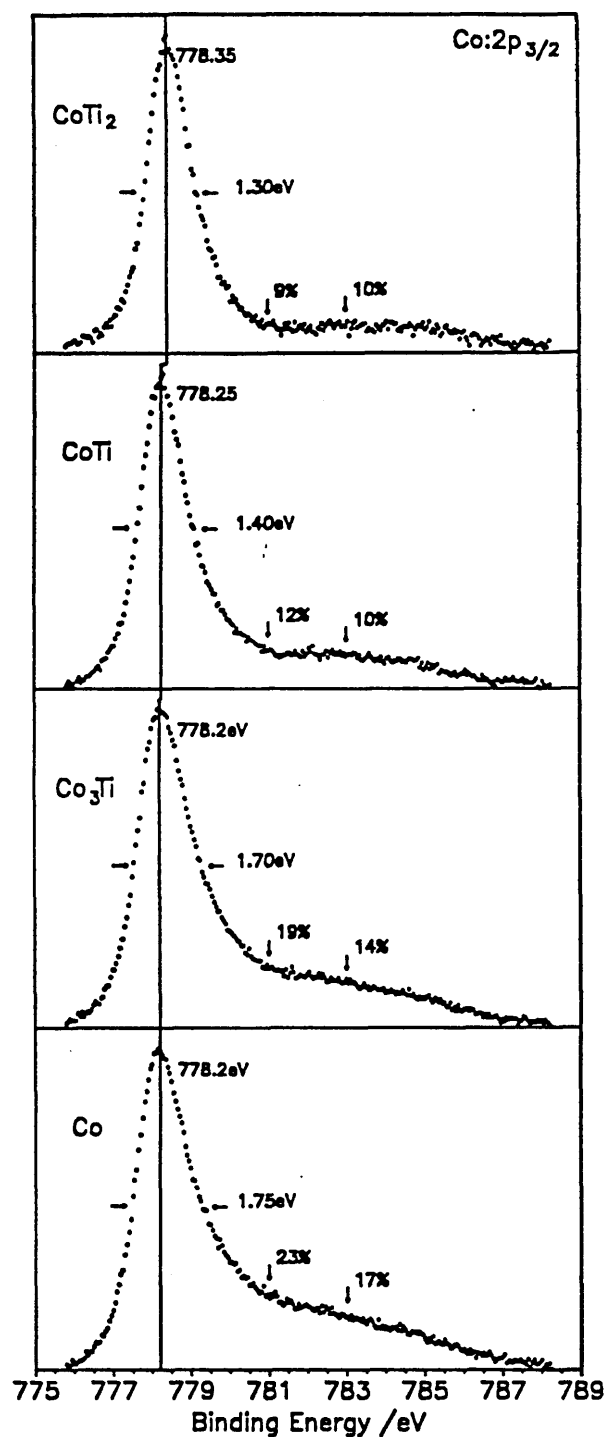


Figure 7.12: Mg $K\alpha_{1,2}$ XPS spectra of the Co:2p_{3/2} region of the annealed Co-Ti alloys and Co metal. A straight-line background (775→788eV) has been subtracted from all spectra. The relative satellite intensity is marked at two arbitrary positions (781 and 783eV) and shows a gradual decrease with Co dilution. Measurement of the FWHM of the main intensity shows some narrowing with Co dilution.

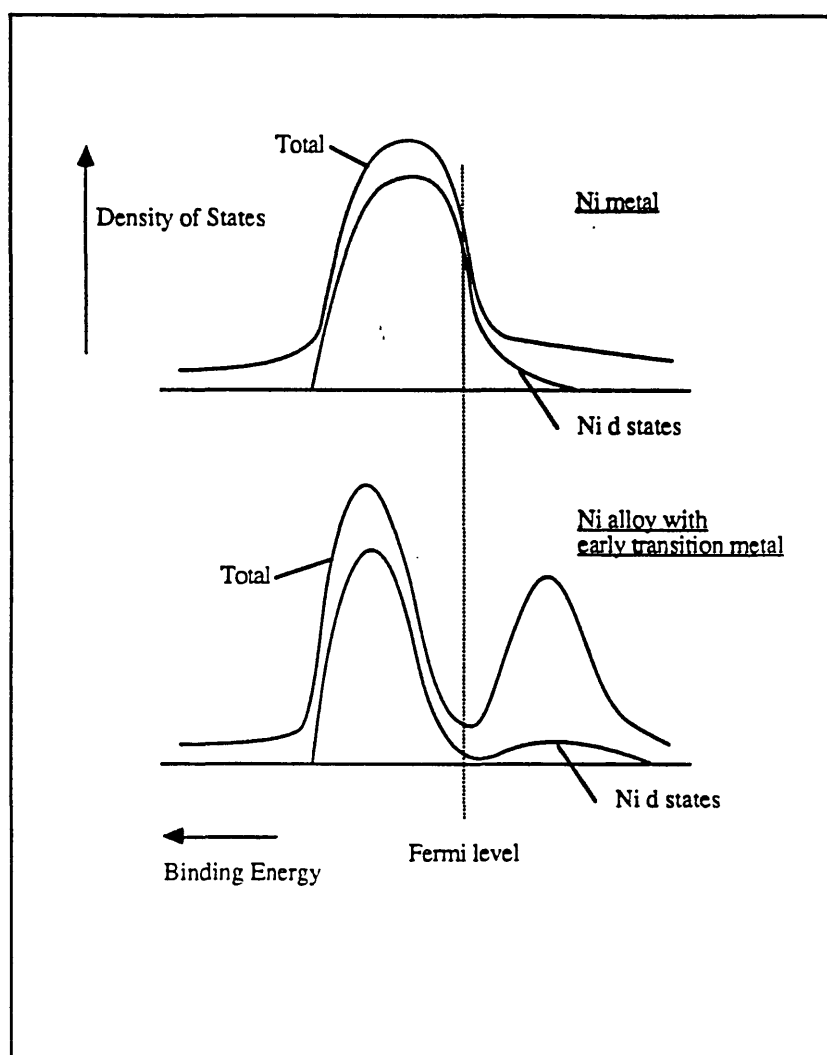


Figure 7.13: Band picture proposed by Fuggle *et al*^{7.14, 7.15, 7.16} for Ni and Ni alloyed with an early transition metal (M). The narrow d band overlies a broad sp band. The Ni d band contains 9.4 electrons in Ni metal. Mixing of the Ni and M d bands in the alloy fills the Ni band further, resulting in a shift of the occupied d band maximum away from E_F and a decrease in DOS at E_F .

suggested that the degree of mixing of the metal d bands is greatest when the electronegativities of the atoms are not too dissimilar. In this way, the Ni band can become filled *without* the need to introduce charge transfer.

In the DOS calculations of CoTi^{7.2, 7.3, 7.4}, there is a close correspondence between the position of maxima in the Co and Ti partial 3d DOS, both above and below E_F . This is good evidence for the mixing of Co and Ti orbitals. Furthermore, the difference in Co and Ti electronegativities is sufficiently small that orbital interaction is expected to be favourable. If the results on Ni and Ni alloys can be extended to Co and Co alloys, then by analogy, it seems probable that the nominal $d^7 4s^2$ configuration of the free Co atom will be replaced by a configuration between $3d^8 4s^1$ and $3d^9$ in Co metal. Hence, the final states corresponding to screened and unscreened intensity seen in the core level spectra may actually correspond with d^8 - and d^9 -like electron configurations.

If it can be assumed that the intensity of the Co core level satellite is purely intrinsic, then the relative weight of d^8 and d^9 satellite structure provides information about the number of holes in the d band. The decrease in satellite structure in the dilute alloys is consistent with Co:d band filling proposed by Fuggle *et al* although the experimental resolution of the valence band spectra presented here does not allow changes in bandwidth to be measured.

7.7 Conclusions

An examination of core and valence XPS spectra of Co-Ti alloys has shown that upon increasing Co dilution in the alloy (going through the series $\text{Co} \rightarrow \text{Co}_3\text{Ti} \rightarrow \text{CoTi} \rightarrow \text{CoTi}_2$),

(i) the valence band maximum shifts away from E_F and the DOS at E_F decreases, consistent with the movement of the d band away from the Fermi level.

(ii) the position Co:2p core peaks shift slightly to higher binding energy. The Ti:2p peaks are considerably shifted to higher binding energy with respect to elemental Ti in all the alloys but the shift is greatest in the Ti poor alloy

Co₃Ti. The shifts relate to the thermodynamic contributions of dissolving an impurity atom in the alloy matrix.

(iii) the Co:2p peak becomes more symmetrical. This can be understood in terms of a decreased DOS at E_F reducing the probability of small energy electron-hole pair excitations across the Fermi edge.

(iv) the satellite structure associated with the Co:2p core levels becomes weaker and more intensity is directed into the main 'screened' peak. This suggests that the screening mechanism is becoming more efficient in the Co-rich alloys and indicates that the Co d band is becoming filled.

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Erratta

page 42: Paragraph 2. "Steps in background intensity occur to the low binding energy side of a peak as the result of inelastically scattered electrons reaching the surface..." should read "Steps in background intensity occur to the *high* binding energy side of a peak as the result of inelastically scattered electrons reaching the surface..."

page 42: Paragraph 3. "...the electron orbiting the nucleus possesses an associated angular momentum l which can take values 0,1,2,3..." should read "...the electron orbiting the nucleus possesses an associated angular momentum *quantum number* l which can take values 0,1,2,3..."

page 52: Equation 2.8 should read

$$n\lambda = d \sin\Theta$$

page 79: Paragraph 2. "...the relationship for the electron mean free path $\lambda = KE^{0.75}$..." should read "...the relationship for the electron mean free path $\lambda \propto KE^{0.75}$..."

page 152: Paragraph 1. "The maximum amount of energy transferred to an atom M_B during collision with an incident atom M_A is $4M_A M_B / (M_A + M_B)$..." should be replaced by "The maximum *fraction* of energy transferred to an atom *of mass* M_B during collision with an incident atom *of mass* M_A is

$$E_B/E_A = 4M_A M_B / (M_A + M_B)^2$$

where E_B is the energy transferred to molecule B and E_A is the initial energy of particle A ."