ELECTRON EMISSION, SURFACE COMPOSITION AND ADSORPTION PHENOMENA OF METALS AND ALLOYS

PHOTOELECTRIC EMISSION OF CLEAN AND CO-COVERED FILMS OF Au-Pt, Ag-Pd AND Pt-Ru ALLOYS AND THEIR COMPONENTS

R. BOUWMAN

ELECTRON EMISSION, SURFACE COMPOSITION AND ADSORPTION PHENOMENA OF METALS AND ALLOYS

ELECTRON EMISSION, SURFACE COMPOSITION AND ADSORPTION PHENOMENA OF METALS AND ALLOYS

PHOTOELECTRIC EMISSION OF CLEAN AND CO-COVERED FILMS OF Au-Pt, Ag-Pd AND Pt-Ru ALLOYS AND THEIR COMPONENTS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN
DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN
DE RECTOR MAGNIFICUS DR. C. SOETEMAN,
HOOGLERAAR IN DE FACULTEIT DER LETTEREN,
TEN OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT
TE VERDEDIGEN OP WOENSDAG 4 NOVEMBER 1970
TE KLOKKE 16.15 UUR

DOOR

ROBERT BOUWMAN

GEBOREN TE SEMARANG
N.O. INDIË (THANS INDONESIË)
IN 1940

1970
DRUKKERIJ BRONDER-OFFSET N.V.
ROTTERDAM

PROMOTOR: PROF. DR. W.M.H. SACHTLER

Voor Maret

Aan mijn ouders

CONTENTS

page

PREFACE

Chapter I GENERAL INTRODUCTION 13
- 1. Heterogeneous catalysis and electron emission 13
- 2. Alloys and catalysis 14
- 3. The work function of alloys 17
- 4. Outline of this study 18
- References 19

Chapter II PHOTOTUBES FOR STUDYING ELECTRON EMISSION FROM THIN FILMS SINTERED IN THE RANGE 78-925K IN ULTRA-HIGH VACUUM 21
- Summary 21
- 1. Introduction 22
- 2. Tube I 23
  - 1. Description and construction 23
  - 2. Operation and features of tube I 25
- 3. Tube II 27
  - 1. Description and construction 27
  - 2. Operation 30
- 4. Aknowledgements 31
- References 31

Chapter III PHOTOELEKTRISCHE UNTERSUCHUNGEN DER ADSORPTION VON KOHLENMONOXYD AUF PLATINFILMEN 32
- 1. Zusammenfassung / Summary 32

page

Einleitung 32

Experimenteller Teil 33

1. Messanordnung 33

2. Durchführung und Auswertung der Messungen 34

Ergebnisse 34

Diskussion 36

Literatur 38

Chapter IV 1. PHOTOELECTRIC DETERMINATION OF THE WORK FUNCTION OF Ru-FILMS AS A FUNCTION OF SINTERING TEMPERATURE (78°-925°K) 39

Summary 39

1. Introduction 40

2. Experimental 41

3. Results 43

4. Discussion 45

5. Aknowledgements 49

References 49

2. PHOTOELECTRIC DETERMINATION OF THE EQUILIBRATION OF METAL AND ALLOY FILMS 51

1. Introduction 51

2. Results 52

References 54

Chapter V PHOTOELEKTRISCHE UNTERSUCHUNGEN DER ADSORPTION VON KOHLENMONOXYD UND XENON AUF UNGEORDNETEN UND GEORDNETEN RUTHENIUMFILMEN 55

Zusammenfassung 55

Summary 56

1. Einleitung 57

2. Experimenteller Teil 59

3. Ergebnisse 61

4. Diskussion 65

Literatur 68

page

Chapter VI PHOTOELECTRIC DETERMINATION OF THE WORK FUNCTION OF GOLD-PLATINUM ALLOYS 69
Summary 69
1. Introduction 70
2. Experimental 73
3 a. The phototubes 73
b. Metal deposition 76
c. Analysis of the bulk composition 77
d. Determination of the work function and emission constant 78
3. Results 79
a. Experiment I 79
b. Experiment II 81
c. Experiment III 83
d. Experiment IV 86
4. Discussion 89
5. Conclusions 92
Aknowledgements 93
References 93

Chapter VII INVESTIGATION OF THE SURFACE COMPOSITION OF Ag-Pd ALLOY FILMS 95
1. Introduction 95
2. Experimental 96
3. Results 96
a. Sintering phenomena of the pure metal films 96
b. Adsorption of carbon monoxide by the pure metal films 97
c. Equilibration of alloy films in ultra-high vacuum and in the presence of CO 99
4. Discussion 105
5. Conclusions 110
References 110

page

Chapter VIII INVESTIGATION OF THE SURFACE COMPOSITION OF Pt-Ru ALLOY FILMS 112
1. Introduction 112
2. Experimental 114
3. Results 115
4. Discussion and Conclusions 120
References 122

Chapter IX GENERAL DISCUSSION 124

SUMMARY 135

SAMENVATTING 139

PREFACE

This thesis consists of a number of chapters, some of these being publications or manuscripts of publications.

Chapters VII and VIII describe unpublished work on silver-palladium and platinum-ruthenium alloys.

The general introduction merely provides a framework in which the rôle of the work function in heterogeneous catalysis is emphasized.

The specific subjects in the different chapters are introduced and discussed separately.

The general discussion provides the connective text necessary to show the whole study as a coherent system of interconnected parts.

The author is indebted to the editors of the respective scientific journals for their permission to reproduce the original texts submitted to them.

Chapter I

GENERAL INTRODUCTION

The work described in this thesis deals with the surface composition of three alloy systems, each of which is of interest for heterogeneous catalysis.

The experimental technique employed to reveal the surface composition of alloys is the monitoring of the emission of photoelectrons and determination of the work function[*].

In this chapter, the importance of the work function for heterogeneous catalysis and in particular for catalysis by alloys, is emphasized.

1. Heterogeneous catalysis and electron emission

Heterogeneous catalysis by metals and electron emission from metals have an important tangent plane: some of the basic problems of heterogeneous catalysis are concerned with the electron transfer through the interphase between the solid and the reactive gas or liquid phase, in the formation of a chemisorption complex.

The basic electronic parameters which are involved in the process of electron transfer are the work function of the catalyst (metals or alloys in our case) and the ionization potential or electron affinity of the adsorbing molecule.

---

[*] By definition, the work function Φ of a metal corresponds to the energy required to bring an electron from the Fermi level of the conduction band to the field free vacuum near the surface.

Nevertheless, a simple correlation between these electronic parameters and parameters like heat of adsorption does not exist at present; the data on the work function of metals collected in the past decade, using modern ultra-high vacuum technique show that the work function of metals and the heat of adsorption or the catalytic activity are not correlated in a simple way.

Gold and platinum e.g. have very similar work functions but they differ vastly in chemisorptive and catalytic behaviour[1].

Still, the work function is an important tool for research in heterogeneous catalysis because it is highly sensitive to physical changes of the surface and to the presence of adsorbed molecules.

The change of the work function brought about by the adsorption of gases[*], specific for a metal-gas pair, provides us - with a high sensitivity - information on :

1. Adsorption of gases and interaction between adsorbed gases in the adsorbed state.
2. The surface composition of alloys (see Paragraph 3).

2. Alloys and catalysis

Alloys have always intrigued workers in the field of catalysis by metals because alloys provide the opportunity to vary lattice parameters and electronic properties of metal catalysts continuously.

The variation of the lattice parameters in the solid forms the basis of the so-called "geometric factor" put forward by several authors[2-6]. According to their viewpoint, the activation energy of adsorption is

---

*) Many authors use the term "Surface Potential" in relation to changes of the work function of the metal by the adsorption of gases. By definition, the surface potential:

$$S.P. = \frac{-\Delta\Phi}{e} = (\Phi_o - \Phi)/e$$

wherein Φ_o is the work function of the clean metal, Φ is that of the covered metal and e is the elementary charge. The change of the work function $\Delta\Phi$ is related to the dipole moment μ of the adsorbed molecule .(See for instance ref. 28) dependent on the spacing of the metal atoms in the surface lattice. Thus one may hope to achieve optimal catalytic activity by appropriately matching the interatomic spacing in the metal surface lattice to bond lengths of reactive species.

The relation between collective electronic properties of metals and alloys and their catalytic activity forms the basis of the so-called "electronic factor".

Dowden[7] stressed the importance of d-band vacancies for catalysis by metals. His original theory is based on the assumption, that processes on metal and alloy surfaces can be described in terms of electron transfer and are therefore characterized by typical electronic properties of the solid state.

According to Dowden, the catalytic activity of a transition metal possessing an unfilled d-band would be reduced to zero by alloying it with a sufficient amount of a typical sp-metal capable of filling the holes in the d-band. In other words, e.g. the magnetic susceptibility of metals and alloys should be indicative of catalytic activity.

Boudart[8] and Beeck[9] presented evidence in favour of the electronic hypothesis for single metals; Schwab[10] formulated a number of postulates to apply it to alloys. There seems to be a general agreement that those experiments are the most promising, in which alloys are employed, where the d-band vacancies of one metal can be filled continuously. Thus alloys of the group VIII-transition metals with one of the group I-transition metals are frequently chosen.

The copper-nickel system is one of these systems which has been studied extensively. According to the electronic concept, the catalytic activity of Cu-Ni alloys must be zero for those bulk compositions having a filled d-band. This was indeed found by Schwab[10], Reynolds[11] and Rienäcker[12]. Rienäcker[13], Hall[14] and Russell[15], however, presented experimental evidence which seems to indicate that alloys which should be inactive according to the electronic concept, in fact are even more active than pure nickel.

Around 1960, the "Dutch School"[16] provided a new insight into the nature of the chemisorption bond. Fahrenfort, van Reijen and Sachtler[17,18] showed, that stability and ease of formation of the surface complexes are related to the heat of formation of the corresponding chemical compound.

Extensive studies on the surface composition and catalytic activity of equilibrated Cu-Ni alloys have made it abundantly clear that the supposed relation between d-band vacancies of alloys and chemisorption respectively catalysis is extremely doubtful (Sachtler, Dorgelo, Jongepier and van der Plank[1,19-23]).

They proved that a wide range of Cu-Ni alloys prepared by sublimation and subsequent sintering at 473°K in ultra-high vacuum is characterized by a constant surface composition. This is copper-rich and contains an amount of nickel given by the copper-rich edge of the miscibility gap of the T-x phase diagram.

The authors[19,20] interpreted their results in terms of thermodynamics and kinetics and developed a model of equilibration of Cu-Ni alloys. According to them, copper envelops nickel crystallites by enhanced surface diffusion in the initial stage. As a much slower process, the composite crystallites, consisting of nickel kernels surrounded by copper jackets, equilibrate by volume interdiffusion. The copper jacket forming the vacuum-exposed phase is thereby enriched with nickel up to an amount (about 25 at% Ni) which is dictated by the copper-rich edge of the miscibility gap of the system.

The results of catalytic test reactions[23], carried out in the presence of these alloy films, can be summarized as follows:

1. The activity and activation energy for the reaction under study (hydrogenation of benzene) are the same for all alloys which have an overall composition between about 25 and 98 at% Ni.
2. The nickel content in the surface of the same range of alloys is about 25 at%.
3. The activation energy for the reaction on all alloys which have the same copper-rich surface is 25 Kcal.mole^{-1} and that on pure nickel is 12 Kcal.mole^{-1}.

The consequences of these results for catalysis by alloys are:

1. Alloys have surface compositions which can differ considerably from the overall composition.
2. The individual character of one metal, viz. nickel is preserved, though modified, even in an environment rich in the other metal.

The first consequence opens a totally new field for exploration on alloys, the second abandons the collective electronic band model and forces us to focus our attention on the individual character of atoms in the surface.

3. The work function of alloys

The work function of a metal is a characteristic surface parameter and can therefore be applied to the characterization of the surface of an alloy. A theory of the work function of alloys does not exist at present. One is not yet able to understand the electronic properties displayed by the surface as indicated by experiments.
However, promising results[19,20] seem to be obtainable by using measurements of the electronic work function in determining the surface composition of alloys. This is still difficult when only the work function of the bare alloy is available, in particular because the work function, when plotted versus the composition, shows minima in some cases[19,24-26], so that a linear interpolation between the characteristic work functions of the pure metals is meaningless.
However, the method of "surface titration", introduced by Sachtler and Dorgelo[19], enables us to make a better approximation of the surface composition.
This method is based on the principle that the work function of most metals is changed by the adsorption of a gas.
The change of the work function possesses a characteristic value for any metal-gas combination. For Cu-Ni alloy films, Sachtler and Dorgelo[19] used carbon monoxide as the "titration agent" because it was known that this gas is chemisorbed readily by nickel and not by copper under relatively low pressures and at room temperature.
The above authors found that $\Delta\Phi$, brought about for all equilibrated alloy films having gross compositions within the miscibility gap, is about +0.1 eV, whereas that of pure nickel is above +1 eV[27].
From the constant work function of the clean, equilibrated alloys and from the constant, small change of Φ_{alloys}, brought about by CO-adsorption they concluded that:

1. These alloys possess constant surface compositions.

2. The surface composition is copper-rich.

This method is unique and although considerable theoretical effort is necessary to arrive at quantitative expressions to correlate the $\Delta\Phi$-values of alloys with precise surface compositions, even so it opens a completely new field of research on alloys.

Among other methods which restrict themselves to the study of surface layers, Auger seems to be a powerful tool.

The work presented in this thesis deals with the surface compositions of three alloy systems, viz. gold-platinum, silver-palladium and platinum-ruthenium. Each of these systems has been selected carefully so as to obtain as much information as possible and with relevance to heterogeneous catalysis.

The reader is referred to the relevant chapters for a detailed argumentation for the choice of these alloy systems.

4. Outline of this study

In the first three parts of the general introduction we have indicated how the significance of the work function for chemisorption and catalysis has changed in the course of time: first it was considered to be a physical property, with which the electronic interaction of metals with adsorbing molecules might be described. Now the work function is put to use to characterize the surface compositions of alloys. Moreover, the work function is still useful for studying adsorption complexes.

The present study concerns the elucidation and rearrangements of the surface of Au-Pt, Ag-Pd and Pt-Ru alloys. It is described in the following chapters:

Chapter II describes the most important tools used in this research. Two new phototubes are described, which have been especially designed and constructed to overcome the experimental problems, given by the nature of the systems. Techniques used commonly in this type of work have not been discussed separately in this thesis.

Adequate descriptions are given in the references 28-31.

Chapter III deals with the chemisorption of carbon monoxide by pure platinum films as a function of the temperature of presintering.

Chapter IV consists of two parts: the first deals with the work function of clean ruthenium films as a function of the temperature of presintering and the second part deals with general considerations on the equilibration of metal and alloy films.

Chapter V describes a study of the change of the work function of ruthenium films, brought about by the adsorption of xenon and carbon monoxide as a function of the temperature of presintering of the film.

Chapter VI presents results on the surface composition of equilibrated alloys of gold and platinum and enrichment of their surfaces with platinum after prolonged treatment with CO.

Chapter VII is concerned with the surface composition of silver-palladium alloys in the absence and presence of CO.

Chapter VIII provides results on a study of the surface composition of platinum-ruthenium alloys in the absence and presence of CO.

Chapter IX contains a general discussion on the complete work and it provides the necessary connective text for understanding the cohesion between the separate studies of this thesis.

References

1) W.M.H. Sachtler and P. van der Plank, Surface Sci. 18, 62 (1969).
2) A.A. Balandin, Z. phys. Chem. 132, 289 (1929).
3) A. Sherman and H. Eyring, J. Am. Chem. Soc. 54, 2661 (1932).
4) G.H. Twigg and E.K. Rideal, Trans. Faraday Soc. 36, 533 (1940).
5) O. Beeck, A.E. Smith and A. Wheeler, Proc. Roy. Soc. A177, 62 (1940).
6) A.A. Balandin, Adv. Catalysis 10, 96 (1958).
7) D.A. Dowden, J. Chem. Soc. 242 (1950).
8) M. Boudart, J. Am. Chem. Soc. 72, 1040 (1950).
9) O. Beeck, Disc. Faraday Soc. 8, 118 (1950).
10) G.M. Schwab, Disc. Faraday Soc. 8, 166 (1950).
11) P.W. Reynolds, J. Chem. Soc. 265 (1950).
12) G. Rienäcker and G. Vornum, Z. anorg. allg. Chem. 283, 287 (1956).
13) G. Rienäcker and S. Unger, Z. anorg. allg. Chem. 274, 47 (1953).
14) W.K. Hall and P.H. Emmett, J. Phys. Chem. 63, 1102 (1959).

15) W.W. Russell and P.B. Shallcross, J. Am. Chem. Soc. 81, 4132 (1959).

16) J.M. Thomas and W.J. Thomas, "Introduction to the principles of heterogeneous catalysis", p. 314, Academic Press, London (1967).

17) J. Fahrenfort, L.L. van Reijen and W.M.H. Sachtler, Z. Elektrochem. 64, 216 (1960).

18) J. Fahrenfort, L.L. van Reijen and W.M.H. Sachtler, "The mechanism of heterogeneous catalysis", ed. by J.H. de Boer et al., p. 23, Elsevier, Amsterdam (1960).

19) W.M.H. Sachtler and G.J.H. Dorgelo, J. Catalysis 4, 654 (1965).

20) W.M.H. Sachtler and R. Jongepier, J. Catalysis 4, 665 (1965).

21) W.M.H. Sachtler, G.J.H. Dorgelo and R. Jongepier, Proceedings of the Intern. Symposium on "Basic Problems in Thin Film Physics", Clausthal-Göttingen p. 218 (1965).

22) P. van der Plank, Thesis (1968), Leyden University, the Netherlands.

23) P. van der Plank and W.M.H. Sachtler, J. Catalysis 12, 35 (1968).

24) B.Ch. Dyubua, O.K. Kultashev and L.V. Gorshkova, Soviet Physics, Solid State 8, 882 (1966).

25) K.P. Gurov and A.I. Pekarev, F.M.M. 17, 500 (1964).

26) B.Ch. Dyubua, O.K. Kultashev and I.A. Tsyganova, Radiotekhn. i. ēlektron. 9, 2061 (1964).

27) A. Eberhagen, Fortschr. Physik. 8, 245 (1960).

28) J.H. de Boer, 'Electron Emission and Adsorption phenomena", Cambridge, At the University Press, (1935).

29) H. Simon and R. Suhrmann, "Der lichtelektrische Effekt und seine Anwendungen", Springer Verlag, Berlin (1958).

30) Th.G.J. van Oirschot, Thesis (1970), Leyden University, the Netherlands.

31) R.W. Roberts and Th.A. Vanderslice, "Ultrahigh vacuum and its applications", Prentice-Hall Inc. Englewood Cliffs, N.Y. (1963).

Chapter II

PHOTOTUBES FOR STUDYING ELECTRON EMISSION FROM THIN FILMS SINTERED IN THE RANGE 78 - 925 K IN ULTRA-HIGH VACUUM*

by

R. Bouwman and F.C. Kauffeld

Afdeling Heterogene Katalyse
Gorlaeus Laboratoria, Rijksuniversiteit, Leiden
the Netherlands

Summary

Two phototubes were developed in which thin films (metals, alloys, semi-conductors)deposited on glass and quartz supports can be sintered at temperatures between 78° and 1,000°K without impairing ultra-high vacuum conditions.

Tube (I) (78° - 600°K) has as its essential feature a shutter for protecting the cathode support during degassing and pre-evaporation of the metal to be vapour-quenched.

Tube (II) (300° - 1,000°K) is characterized by a simply movable quartz cathode support, which is exposed entirely to ultra-high vacuum. This cathode support, after having been subjected to a severe preliminary degassing procedure, allows sintering of films up to 1,000°K without contamination of their surface.

---

* Submitted for publication to the Journal of the Scientific Instruments (Journal of Physics E).

1. Introduction

Photoemission from solids and liquids can be used to obtain information on bulk and surface properties, including the work function of the material under study. Photoemission data are valuable for a better understanding of specific problems of adsorption, heterogeneous catalysis and (doped) semi-conductors. Other phenomena such as surface diffusion and -sintering processes can also be detected photoelectrically (Bouwman, 1970).
Techniques involving thin film preparation (by sublimation, sputtering, chemical vapour deposition or wet plating) have gained growing interest in the last ten years. Thin films have the advantage of a high ratio between surface exposed atoms and non-exposed ("volume"), atoms and a considerable amount of lattice imperfections.
Films, therefore, may be subjected more easily to equilibration processes (e.g. low temperature alloying, doping, etc.) than macroscopic samples. The support of films is of importance, as it may induce epitaxial growth during deposition. Metal supports can interfere seriously by alloying with metal films deposited on them. Glass substrates, being preferable for studying polycrystalline metal and alloy films, are limited by their thermal instability and by increased porosity at higher temperatures.
In this paper, phototubes are described which are used for investigation of vapour-quenched metal and alloy films. These designs (with minor alterations) can also be used for numerous other purposes.
Alloys of metals having high melting points are difficult to equilibrate, also as films. As it should be possible to study thin metal and alloy films in ultra-high vacuum (10^{-10}Torr or lower) in order to obtain reliable information on bulk and surface properties, even after sintering at temperatures up to about 1,000^{o}K, we developed two types of phototubes:

1. Tube (I) has been designed for low temperature vapour-quenched films and allows sintering between 78^{o} and 600^{o}K.

2. Tube (II) has been designed for films which were to be sintered up to 1,000^{o}K.

2. Tube (I)

2.1 Description and construction

This tube (Fig. 1) consists of a pyrex dewar type part (1), terminating

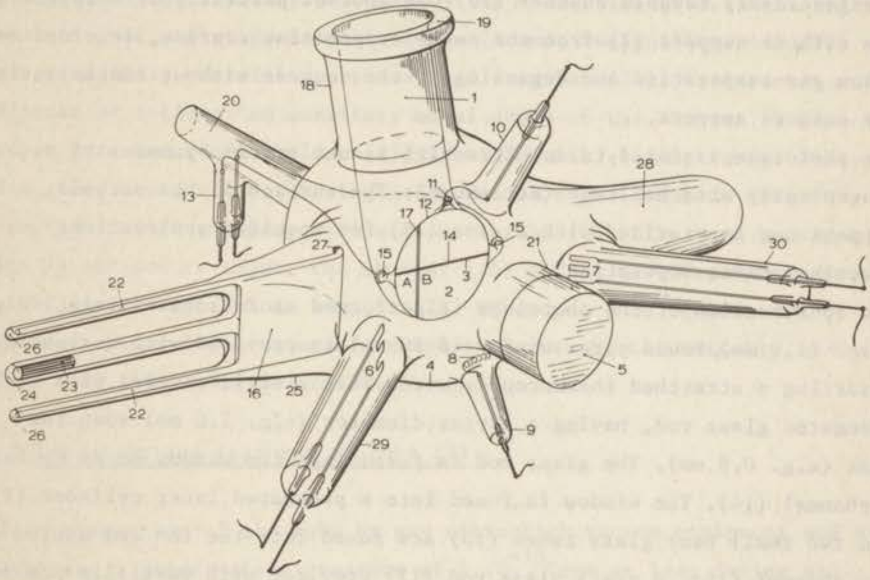


Figure 1

Phototube I.

in a polished flat cathode support (2) provided with an embedded thermocouple (3). The dewar part is mounted within pyrex housing (4), equipped with optical quartz window (5), metal evaporation sources (6, 7) and wound platinum wire (8) embedded in the interior of the housing and connected to a fused tungsten anode lead (9). A fused tungsten cathode lead (10) is connected with thin platinum wire, wound around a small glass rod (11), which is fused into the edge of the cathode support. This platinum wire makes electrical contact with a thin layer of platinum paste, baked as a narrow semi-circular ring (12) into the periphery of the cathode support. Two fused tungsten leads (13) are connected with a thermocouple (3).

Thermocouple wires enter a channel (14) in the cathode support (2) through fused, bent tubes (15). These serve to prevent electrical contact between the thermocouple and the metal film to be evaporated onto the cathode support.

A magnetically movable shutter (16) can protect partially or completely the cathode support (2) from the metal evaporation sources, in order to allow pre-evaporation and degassing of the sources without contaminating the cathode support.

The phototube is fused to an ultra-high vacuum system by means of a conveniently attached tube (not shown). The surface of the cathode support can be provided with a slot (17) for specific applications described under "Operation".

The construction of the phototube is performed as follows: a relatively thick (4.0 mm), round pyrex window (Ø 60 mm) is provided with a slot for inserting a stretched thermocouple wire. This slot is covered with an elongated glass rod, having a larger diameter (e.g. 2.0 mm) than the slot (e.g. 0.8 mm). The glass rod is fused into the window so as to leave a channel (14). The window is fused into a preshaped inner cylinder (1) and two small bent glass tubes (15) are fused into the in- and outlet of the channel (14). A small glass rod (11) provided with partially embedded platinum wire (Ø 0.30 mm) is attached to the edge of the window.

After this, the surface of the window is abraded and polished to form a flat cathode support (2). A vertical slot (17) is sawn, if desired, in the surface of the support (2). Platinum paste N 758 (Johnson, Matthey & Co, Ltd. London) is applied and baked (1,000°K) into the glass and into the surface of the rod (11).

A stretched thermocouple (Ø 0.30 mm) is slipped into the channel (14).

The finished dewar part is now inserted into an outer cylinder (18) which has partly been formed into a spherical shape and the cylinders are fused together (19). A tube (20) is fused to the spherical part of the outer cylinder in such a way, that it is perpendicularly and centrally directed towards the back of the cathode support.

This tube (20) is used among others as a grip for insertion into a glass lathe in order to fuse the quartz-pyrex transition (21) properly to the phototube (the drawing, which does not give the exact appearance of the actual phototube, is transformed to show these details more clearly). The spherical bottom portion of the cylinder (18) is now closed and pyrex-quartz transition (21), provided with optical "Suprasil" quartz window (5) (Ø 50.0 mm), is attached to the phototube in such a way, that window (5) and cathode support (2) form top and bottom of an imaginary cylinder, which is partly embodied by the transition (21). Shutter (16) consisting of a flat pyrex plate (60 x 75 mm), two guiding rods (22) and drive rod (23), containing a glass-clad iron bar (24), is inserted and adjusted as follows: an auxiliary metal dummy of the shutter is used for proper attachment of a holder (25) provided with sliding tubes (26). Then glass shutter (16), having its terminal edge (27) bent over 90°, is inserted through an open, oval wide bore tube (28). The bent terminal edge is abraded to adjust the shutter (16) in the best way with respect to the surface of cathode support (2). Thereupon tube (28) is sealed and can be reopened later to enable removal of the shutter. Finally, tubes (29), (30), (9) and (10) are fused.

2.2 Operation and features of tube (I)

After evacuation of the tube by any ultra-high vacuum equipment and after obtaining a steady-state pressure of 5.10^{-10}Torr or less during slow evaporation of the metals, shutter (16) is withdrawn and the metals are evaporated onto support (2), which can either be cooled (e.g. by means of liquid nitrogen) or heated by means of a small, removable furnace fitting the backside of the cathode support. If two different metals are evaporated, a properly aligned glass or metal shield can be attached to one of the tungsten leads of one of the metal sources in such a way (not shown), that the metal sources are prevented from "seeing" each other.

As a consequence of the geometric set-up of two different metal sources with respect to the cathode support, the condensed bimetal film will have a horizontal concentration gradient.

This enables one to study a plurality of alloy compositions under, otherwise, identical conditions. (A modification of this phototube which allows preparation of a composite film, consisting of strips of the pure metals, and an intermediate concentration gradient is described elsewhere (Bouwman, 1970)). An electrometer is electrically connected via cathode output (10) to the condensed metal film and a positive accelerating voltage is applied to the anode.

Monochromatic light which has been focussed in the form of a narrow image of a vertical slit is directed onto any desired location of the photocathode. The experimental data are evaluated by known methods (for extensive results on alloy films, see Sachtler 1965, and Bouwman 1970).

Tube (I) can also be used for studying metal films as a function of the temperature of sintering and as a function of film thickness (by evaporating from only one metal source).

Also the physical adsorption and chemisorption (Bouwman, 1970) of gases resulting in a change of emission properties can be studied. Well defined desorption measurements may also be carried out due to the presence of the thermocouple, which is located closely behind the film.

Slot (17) may have been inserted for specific studies where lateral diffusion of metal atoms across the surface of the film should be prevented. Due to the presence of this slot the film is separated into two isolated films (A) and (B). This is an important feature: the uncovered glass in slot (17) stops lateral surface diffusion of atoms from film (A) to film (B) or in the other direction. As an example, a study to obtain information on the change of the work function Φ of a metal film (e.g. platinum) after deposition of one to three atomic layers of an other metal (e.g. gold) on top of it, was carried out as follows: platinum was first evaporated onto the entire cathode support from source (6), then shutter (16) was closed to protect only film (A), and subsequently gold was evaporated from source (7) in such a way, that a monoatomic layer of gold was calculated to be present adjacent to slot (17) and three atomic layers on top of the Pt-film adjacent to the right hand edge of cathode support (2).

Before and after deposition the work function of film (A) and three positions of film (B) were determined. The result (Fig. 2) shows clearly that the work function is dictated by the upmost atomic layers: film (A) gives the value of platinum films deposited at $78^{\circ}K$ and sintered at $293^{\circ}K$ (Φ = 5.68 eV) before and after deposition of gold, while all three locations of film (B) corresponding with one, two and

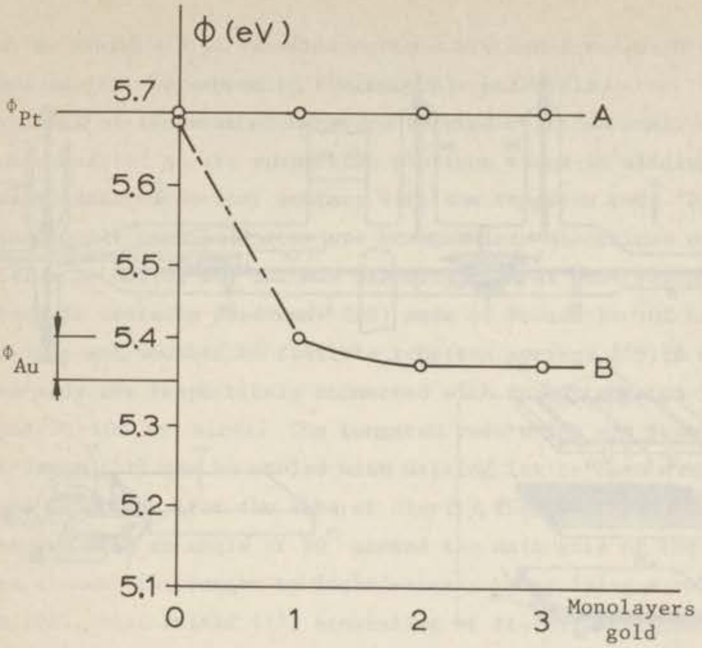


Figure 2
The work function Φ (eV) of a Pt-film (A) before and after deposition of 1, 2, and 3 atomic layers of gold (B) on top of it.

three atomic layers of gold, show gold-values ($\Phi = 5.35 - 5.40$ eV). However, the results on emission properties of metal and alloy films prepared and sintered above 600°K in tube (I) become unreliable due to worse vacuum conditions (which may probably be ascribed mainly to increased porosity of the glass). For alloy films of metals possessing insufficient mobility at temperatures below 600°K, we have developed another phototube (tube II) containing as its essential feature a bakeable quartz cathode which is completely exposed to ultra-high vacuum.

3. Tube (II)

3.1 Description and construction

Tube (II) (Fig. 3) is based on the principles of a phototube used by Sachtler, Dorgelo and Jongepier (1965). It consists of a pyrex housing (1)

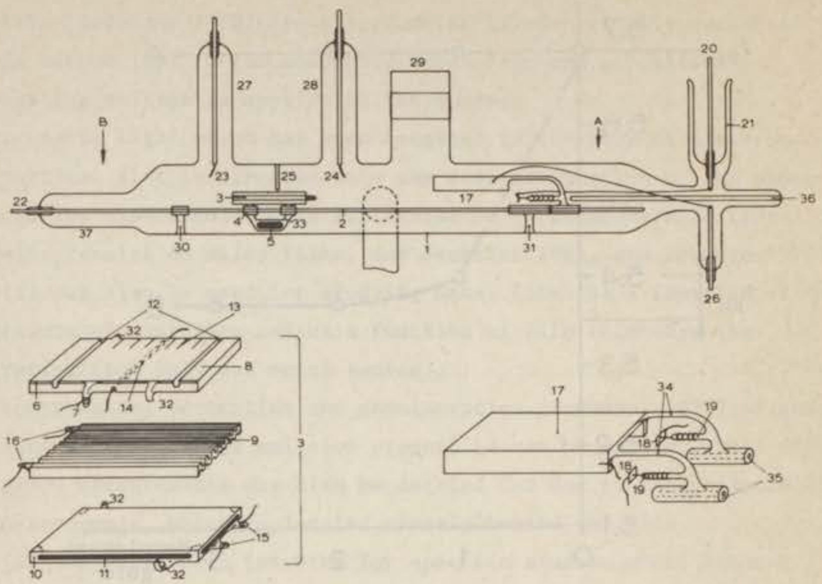


Figure 3

Phototube II.

having a diameter of 50 mm. Through one end two elongated parallel tungsten rods (2) are fused (as Fig. 3 represents the topmost view of the tube these rods are seen as one). A quartz photocathode assembly (3) (shown in detail), sliding over rods (2) on four small tubes (4) is provided with a pyrex-glass clad iron bar (5) to make magnetic operation possible from the outside. The surface of the cathode support is in electrical contact with the tungsten rods through a baked platinum paste strip (6), fused platinum wire (7) and platinum tubes, fused within the pyrex sliding tubes (4). The cathode carrier consists of quartz cathode support (8), quartz oven element (9) containing wound tantalum wire (Ø 0.15 mm) and a backing plate assembly consisting of two quartz slabs (10) and sandwiched platinum foil (11).

Cathode support (8) is provided with two slots (12), calibration marks (13) and a slot for a thermocouple (14). The latter consists of stretched Pt/Pt-10% Rh wire (Ø 0.25 mm) enveloped by a quartz capillary (not shown). The terminals of the thermocouple are connected with bumpers (15) made of the corresponding thermocouple materials.

The terminals of the oven element are secured over two small quartz rods (16) and connected to the respective platinum tubes in sliding tubes (4) in order to make electrical contact with the tungsten rods (2) possible. The thermocouple terminals (15) are brought into electrical contact with the outside by moving the cathode assembly towards heat reflector shield (17), where it contacts dead-ends (18) made of Pt and Pt-10% Rh respectively and mounted on flexible tungsten springs (19)(∅ 0.2 mm wire). The dead-ends are respectively connected with fused tungsten leads (20) by Pt and Pt-10% Rh wires. The tungsten rods which are fused through a small dewar (21) can be cooled with melting ice to form a cold reference junction. (For the sake of clarity, the dewar part in Fig. 3 has been rotated over an angle of 90° around the main axis of the phototube). The oven element is brought to incandescense by applying a voltage at outputs (22). Heat shield (17) consisting of Pt-foil stretched around a quartz mould, serves to conserve the heat of radiation. If it were not there the surrounding pyrex housing would be heated uncontrollably.

Metal evaporation sources (23, 24) are situated on either side of a glass screen (25), the latter having a double function:

1. It prevents the metal sources from "seeing" each other.
2. It is used to protect both terminal zones of the photocathode during evaporation of the metals in order to obtain zones of the pure metals on the extremities of the cathode carrier and an intermediate alloy gradient, slots (12) acting as barriers for lateral diffusion from the alloys across the surface and towards the pure metal zones.

The platinum shield acts as collecting anode and is connected with anode output (26).

The tube is constructed as follows: After attachment of tubes (27) and (28) and pyrex-quartz transition with optical "Suprasil" window (29) to the main housing (1), two supporting means (30, 31) for tungsten rods (2) are fused into the housing.

The cathode sandwich is assembled by fusing upper and lower quartz plate together by quartz connections (32). Tantalum resistance wire is used as heating wire because of its ductility and extremely low vapour pressure.

The undercarriage (33) is an all-pyrex assembly, which is protected from the heat of radiation from the quartz oven by Pt-foil (11). The quartz sandwich is secured to the pyrex undercarriage by quartz, respectively pyrex hooks and eyes (not shown). Heat screen (17) is connected by quartz rods (34) with two quartz tubes (35), which fit tungsten rods (2). It is anchored in the phototube between supporting means (31) and a fused rod (36). Repair of parts of the heat screen assembly can be carried out by cutting the main housing at (A) and removing the dewar part together with the heat screen assembly. Removal or replacement of the cathode assembly can be effected by cutting the main housing at (B) and withdrawing the narrow terminal part (37) together with tungsten rods (2). The cathode assembly can then be removed through the other end of the tube past supporting device (30).

3.2 Operation

This tube requires severe bake-out procedure in order to degas the quartz assembly thoroughly. Therefore the latter is moved into the reflector heat shield and is baked at about 1,000^{o}K whilst the complete vacuum equipment is baked at about 600^{o} - 700^{o}K.

At least a fortnight's period is necessary to degas the quartz assembly satisfactorily in order to allow subsequent sintering of the film at 900^{o}K while maintaining vacuum of 5.10^{-10} Torr or less.

As an example of a well degassed cathode, the steady state pressure in a small ultra-high vacuum equipment (about 2 litres) connected to a 50 l/sec Varian Vacion pump through 1½"-bore tubing is plotted as a function of the temperature of the cathode support (Fig. 4).

The bimetal film is prepared by alternately moving the cathode assembly between a position near to source (23) and near to source (24). In this way one obtains a stratified bimetal film system (a modification of tube (II) enabling simultaneous evaporation of the metal films is obtained by placing sources (23) and (24) closer to each other and dispensing with screen (25)).

Finally the bimetal film is equilibrated by sintering while being hidden in the heat shield assembly.

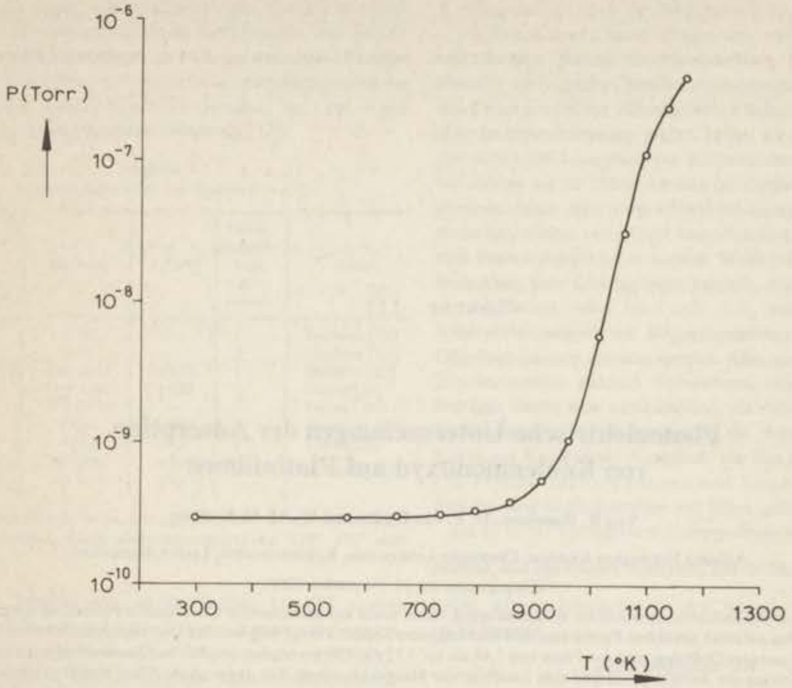


Figure 4

Steady state pressure P (Torr) in Tube (II) as a function of the temperature T (^{o}K) on the quartz photocathode.

4. Acknowledgements: Development of these phototubes was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

References

R. Bouwman and W.M.H. Sachtler, Surface Sci. (1970), in press.

R. Bouwman and W.M.H. Sachtler, J. Catalysis (1970), in press.

R. Bouwman, H.P. van Keulen and W.M.H. Sachtler, Ber. Bunsenges. physik. Chem. 74, 198 (1970).

W.M.H. Sachtler and G.J.H. Dorgelo, J. Catalysis 4, 654 (1965).

W.M.H. Sachtler and R. Jongepier, J. Catalysis 4, 665 (1965).

Chapter III

Photoelektrische Untersuchungen der Adsorption von Kohlenmonoxyd auf Platinfilmen

Von R. Bouwman, H. P. van Keulen und W. M. H. Sachtler

Afdeling Heterogene Katalyse, Chemische Laboratoria, Rijksuniversiteit, Leiden, Niederlande

(Eingegangen am 14. November 1969)

Die Emission von Photoelektronen wurde für spektroskopisch reine, sowie mit adsorbiertem CO bedeckte Platinfilme untersucht, die i. a.
durch Aufdampfen auf einen gekühlten Pyrexträger und nachfolgendes Tempern hergestellt wurden. Die Austrittsarbeit Φ des reinen Platins
steigt mit zunehmendem Ordnungsgrad der Filme von 5,44 bis auf 5,72 eV. Chemisorption von CO bei Zimmertemperatur verursacht an-
fänglich einen Anstieg der Austrittsarbeit und eine Abnahme der Mengenkonstante. Für ungeordnete Filme nimmt die Austrittsarbeit bei
weiterer CO-Zugabe nach Durchlaufen eines Maximums wieder ab. Die Ergebnisse lassen sich durch die Annahme deuten, daß bei Zimmer-
temperatur sowohl Chemi-Adsorption ($\Delta\Phi > 0$) als auch korrosive Chemisorption ($\Delta\Phi < 0$) auftreten, wobei letztere durch Umgruppierun-
gen der Platinatome gekennzeichnet ist.

Films of spec. pure platinum were prepared by deposition from the vapour on a pyrex support, usually cooled with liquid nitrogen. The
photoelectron emission was studied before, during and after chemisorption of CO on these films after they had been subjected to various
degrees of sintering.
The work function Φ of pure platinum was found to increase upon sintering from 5.44 to 5.72 eV.
Chemisorption of CO at room temperature causes initially an increase of the work function Φ and a decrease of the emission constant. For
nonequilibrated films Φ passes through a maximum as a function of the surface coverage of CO.
The results can be interpreted by postulating the occurrence of both chemi-adsorption ($\Delta\Phi > 0$) and corrosive chemisorption ($\Delta\Phi < 0$),
characterized by a rearrangement of platinum atoms.

Einleitung

Die bei der Chemisorption eines Gases an ein Metall gebildeten chemischen Bindungen lassen sich durch verschiedene experimentell zugängliche Größen charakterisieren, z. B. Infrarotspektrum, Austrittsarbeitsänderung oder Widerstandsänderung des adsorbierenden Metalls.

In den Untersuchungen von **Suhrmann** und Mitarbeitern [1–3] spielte dabei die durch Chemisorption hervorgerufene Änderung der Austrittsarbeit Φ eine große Rolle. **Sachtler** [4] wies darauf hin, daß die Austrittsarbeitsänderung $\Delta\Phi$ für die gebildete Chemisorptionsbindung wesentlich symptomatischer ist als etwa die Änderung des Widerstandes aufgedampfter Filme, welche für sehr unterschiedliche Bindungstypen das gleiche Vorzeichen und etwa den gleichen Betrag haben kann.

Ein Gas, dessen Adsorption an Übergangsmetallen durch zahlreiche Autoren [5–8] untersucht wurde, ist das Kohlenmonoxyd. Gründe für die Vorliebe des Experimentators für dies Adsorptiv sind:

1. Die Adsorption ist unter normalen Umständen nicht dissoziativ.
2. Sie ist charakteristisch für das adsorbierende Metall. Kohlenmonoxyd wird an Nickel, Wolfram, Eisen und Platin stark gebunden, ist aber z. B. von Kupfer bei Zimmertemperatur leicht abpumpbar [9–10].
3. Die Infrarotbanden von adsorbiertem CO sind recht intensiv [11].
4. Die Austrittsarbeitsänderungen sind z. B. für die Metalle Ni, Fe, Co, größer als 1 Volt [6–8].

Im Lichte dieser Tatsachen ist es erstaunlich, daß über die Austrittsarbeitsänderungen bei der Chemisorption des Kohlenmonoxyds an Platin nur sehr widersprüchliche Ergebnisse bekannt sind, während für die Platinhomologen experimentelle Daten überhaupt fehlen.

In Tabelle 1 sind die Ergebnisse der Literatur für das System Pt – CO schematisch zusammengefaßt, dabei bedeuten: IR = Infrarot, vibr. cond. = Kontaktpotentialmessungen mit Hilfe der Schwingkondensatormethode von Mignolet, stat. cap. = Kontaktpotentialmessungen mit Hilfe der statischen Methode, FEM = feldelektronenmikroskopische Bestimmungen aus der Neigung der Fowler-Nordheim-Geraden, ret. pot. = mit Hilfe der "retarding potential"-Methode [12].

Tabelle 1
Literaturdaten über das System Pt – CO

Präparat	Methode	$\Delta\Phi$(eV)	Unterscheidbare Zustände	Autor
Film	I. R.	–	1	Eischens [11]
Pt/Al_2O_3	I. R.	–	2	Eischens [11]
Film	vibr. cond.	+0,23	1	Dorgelo [15]
Film	stat. cap.	0 ± 0,01	–	Heyne [20]
Pt/Aerosil	I. R.	–	1	Heyne [20]
Spitze	FEM	+0,68	–	Rootsaert [21]
Spitze	FEM	+0,4	2*)	Lewis [23]
(100)-Fläche	ret. pot.	+0,18	3**)	Morgan [22]
(111)-Fläche	ret. pot.	+0,17		

*) Außerdem physikalische Adsorption ($\Delta\Phi < 0$) unterhalb 50 °K.
**) Unterscheidbar durch Desorptionspeaks bei 130°, 170° und 600 °C.

Wie die Tabelle zeigt, ist das System Pt – CO unseres Wissens bisher noch nicht photoelektrisch untersucht worden. Es ist nicht ausgeschlossen, daß Widersprüche in Tabelle 1 zum Teil auf die unterschiedlichen Meßmethoden zurückzuführen sind. So verfälscht bei der Kontaktpotentialmethode jede Adsorption des Gases an der Bezugselektrode notwendigerweise das Meßergebnis, wenn hierdurch die Austrittsarbeit der Bezugselektrode geändert wird. Bei der feldelektronenmikroskopischen Methode gehen die Flächenelemente niedrigster Austrittsarbeit mit dem stärksten Gewicht ein; die schematische Bestimmung von

$$\Delta\Phi = \Phi_\theta - \Phi_0 \qquad (1)$$

Φ_0 = Austrittsarbeit des reinen Metalls
Φ_θ = Austrittsarbeit des bedeckten Metalls

ist nur dann physikalisch sinnvoll, wenn nach der Adsorption die gleichen Flächenelemente die Emission beherrschen wie vor der Adsorption [13]. Aber selbst wenn dies der Fall ist, beschränkt sich der Aussagewert von Messungen mit dem konventionellen Feldelektronenmikroskop ohne "probe-hole"-Anordnung [13] auf die am stärksten emittierenden Kristallflächen.

Eine wichtige Folgerung, die aus den Daten der Tabelle 1 gezogen werden kann, ist das Auftreten von mehreren nebeneinander vorliegenden Bindungszuständen bei der Adsorption von CO an Platinoberflächen. Das gleiche Ergebnis ist auch für das System W – CO und Ni – CO sichergestellt [14, 15]. Die Ergebnisse von **Eischens** [11] zeigen darüber hinaus eine Abhängigkeit der Pt – CO-Bindungen von der Bereitungsweise der Proben, sie legen daher die Annahme nahe, daß die unterscheidbaren Adsorptionszustände auf verschiedenen Kristallflächen in verschiedenen Verhältnissen gebildet werden. Es ist daher verständlich, daß Platinoberflächen von verschiedener kristallografischer Beschaffenheit nach Bedeckung mit Kohlenmonoxyd auch verschiedene $\Delta\Phi$-Werte ergeben.

Da eine Klärung dieser Fragen uns wesentlich erscheint und darüber hinaus die Untersuchung mehrerer nebeneinander vorliegender Chemisorptionskomplexe seit Jahren zu den Zielen sowohl der Suhrmannschen Schule als auch unserer eigenen Untersuchungen gehört, haben wir in der vorliegenden Arbeit die Adsorption von Kohlenmonoxyd bei Zimmertemperatur an im Ultrahochvakuum aufgedampften Filmen photoelektrisch untersucht. Dabei kam es uns darauf an, durch dosiertes Zulassen von CO die Austrittsarbeit Φ mit zunehmendem Bedeckungsgrad θ zu messen. Wenn bei fortschreitender Bedeckung stets Gleichgewicht herrscht, durchläuft $\Phi = f(\theta)$ ein Maximum oder Minimum, falls nacheinander zwei Adsorptionszustände mit entgegengesetztem Vorzeichen des Oberflächendipols gebildet werden. Aber auch Zustände mit Dipolmomenten gleichen Vorzeichens, aber verschiedenen Betrages lassen sich unterscheiden, da dann bei gradueller Erhöhung des Bedeckungsgrades die Austrittsarbeit eine Kurve mit Knickpunkt durchläuft, wie dies durch **Rudnitskii, Tsjachovskai, Kulkova und Temkin** [16] für den Fall der Sauerstoffadsorption auf Silber gefunden wurde.

Da es in der vorliegenden Untersuchung nur auf das Vorzeichen und die *relative* Änderung der Größe $\frac{d\Phi}{d\theta}$ ankommt, haben wir darauf verzichtet, den Bedeckungsgrad absolut zu bestimmen.

Experimenteller Teil

1. Meßanordnung

Die Photozelle (Abb. 1) bestand aus Pyrex-Glas. Ihre wesentlichen Teile waren: ein Dewarteil (1), der in einer planpolierten Fläche (2) endete, die als Träger für den als Photokathode fungierenden Pt-Film diente, ein planparalleles Quarzfenster (3), stellenweise mit dünnem Platindraht umwickelte Wolfram-Aufdampfwendeln (4) und (5), eine Drahteinschmelzung (6), die zusammen mit einer teilweise in die

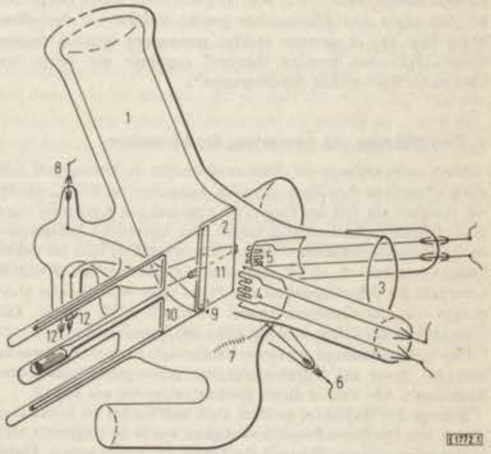


Abb. 1
Photozelle. Erklärung der Zeichen im Text

Glaswand eingebetteten Platinwendel (7) die elektrische Zuführung zu dem als Anode fungierenden, die Innenwand der Zelle bedeckenden Platinfilm bewerkstelligte, eine Einschmelzung (8), die zusammen mit dem in die Kathode eingebetteten und flach geschliffenen Platinblech (9) den Kathodenanschluß ermöglichte, sowie eine Verbindung mit der angeschmolzenen Ultrahochvakuumapparatur. Ferner gestattete ein mit eingeschmolzenem Weicheisenkern versehener und daher magnetisch zu bedienender Schieber (10) eine Abschirmung der Kathode während des Entgasens der Aufdampfwendeln und des Abdampfens eines Teils des Platins zur Entfernung aller flüchtigen Verunreinigungen. Die Kathode konnte sowohl gekühlt werden (z. B. mit flüssigem Stickstoff) als auch geheizt (durch einen kleinen Ofen, der in den Dewarteil eingeführt und gegen den Kathodenträger gedrückt werden konnte). Mit Hilfe des Thermopaares (11), das 0,2 mm unter dem Film in das Glas des Kathodenträgers eingebettet war, konnte die wirkliche Filmtemperatur genau gemessen werden. Das Thermopaar bestand aus einem Platindraht und einem Draht aus einer 90% Pt/10% Rh-Legierung. Der Thermostrom wurde durch die Einschmelzungen (12) nach außen geführt.

Die Innenseite des Dewarteils war mit einem elektrisch leitenden und geerdeten dünnen Zinnoxydfilm bedeckt zur Vermeidung von Haftladungen. Die Außenseite wurde vor jeder Messung mit einer „Aquadag"-Schicht bestrichen. Diese wurde ebenfalls geerdet, um insbesondere Reibungselektrizität während des Siedens von eingefülltem flüssigen Stickstoff abzuführen. Die Photoströme wurden durch ein „Vibron 51A vibrating reed electrometer", der Firma E.I.L., gemessen, das über (8) mit der Kathode verbunden wurde. Die Anode wurde über (6) mit dem positiven Pol einer 90 V-Anodenbatterie verbunden, deren negativer Pol an Erde lag. Licht einer 150 W-Hochdruck-Quecksilberlampe, das durch einen Bausch & Lomb-Gittermonochromator spektral zerlegt wurde, gelangte über ein Spiegelsystem entweder auf die Platinkathode dieser Meßzelle oder auf eine getemperte Tantalkathode in einer selbst gebauten Vergleichszelle.

Zur Vermeidung von Meßfehlern durch unterschiedliche Lichtabsorption wurden die Lichtwege für beide Zellen gleich lang gehalten und identische Quarzfenster für Meß- und Vergleichszelle verwandt.

Die Vergleichszelle war im Institut für physikalische Chemie der Technischen Hochschule Hannover gegen eine Standardzelle geeicht worden, welche zuvor von C. **Wölfing** und H.-G. **Kock** mit großer Sorgfalt gegen eine Thermosäule geeicht worden war. Auf diese Weise liegt den in unserem Institut gemessenen lichtelektrischen Empfindlichkeiten derselbe Standard zugrunde wie denen der Suhrmann-Wedlerschen Arbeitsgruppe*).

2. Durchführung und Auswertung der Messungen

Nach dem Glühen der Aufdampfwendeln in Wasserstoff von etwa 1 Torr und dem Ausheizen der Apparatur bei 450 °C wurde, wie erwähnt, ein Teil des Platins bei abgedecktem Kathodenträger unter Ultrahochvakuum abgedampft. Das eigentliche Aufdampfen des spektralreinen Platins (Johnson Mathey & Co.) fand bei einem Druck unterhalb $5 \cdot 10^{-10}$ und einer Temperatur der Wendeln unterhalb des Schmelzpunktes von Platin statt. Während der Messungen war der Gasdruck immer unterhalb $3 \cdot 10^{-10}$ Torr. Die Schichtdicke der Filme wird auf 250 – 500 Å geschätzt.

Das Kohlenmonoxyd mit einem Reinheitsgrad von 99,99% wurde über ein zuvor auf Ultrahochvakuum gepumptes Dosiersystem eingelassen. Alle Ventile dieses Systems bestanden aus Metall.

Solange der Haftfaktor groß ist, stellt sich hierbei ein konstanter Druck ein. Die Einströmgeschwindigkeit wurde so eingestellt, daß in diesem stationären Zustand der Druck 10^{-6} Torr betrug. Unter diesen Bedingungen darf der Bedeckungsgrad als proportional der Einströmzeit angenommen werden. Das Erreichen desjenigen Bedeckungsgrades, für den diese Annahme nicht mehr zulässig ist, wird an dem Ansteigen des Druckes erkannt.

Die lichtelektrische Empfindlichkeit wird in üblicher Weise aus der bekannten Empfindlichkeit der Vergleichszelle und dem Quotient der gemessenen Photoströme der Meß- und der Vergleichszelle errechnet.

Nach der Theorie von Fowler wird die Abhängigkeit der lichtelektrischen Empfindlichkeit I (in emittierten Elektronen je absorbiertes Photon) von der Lichtfrequenz ν gegeben durch die Beziehung

$$I = M T^2 \left[\frac{\pi^2}{6} + \frac{x^2}{2} - \left(e^{-x} - \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} \cdots \right) \right]. \tag{2}$$

wobei M die Mengenkonstante (Elektronen je Photon je Grad^2) und T die absolute Temperatur ist, während x definiert ist durch

$$x = \frac{h\nu - h\nu_0}{kT} = \frac{E - \Phi}{kT}. \tag{3}$$

Dabei ist $E = h\nu$ die Energie des Photons und Φ die Austrittsarbeit, beide üblicherweise ausgedrückt in eV. Für $x \gg 1$ bzw. $\nu \gg \nu_0$ wird (2) in guter Näherung:

$$I = \frac{M(E - \Phi)^2}{2k^2}. \tag{4}$$

Hieraus folgt, daß man Φ und M grafisch leicht ermitteln kann durch Auftragen von $\sqrt{I}$ gegen E, wobei eine gerade Linie entsteht mit dem Abszissenabschnitt Φ und der Neigung $\sqrt{\frac{M}{2k^2}}$.

Die durch die Streuung der Meßpunkte um die Gerade (4) bedingten Fehlergrenzen betragen jeweils ± 0,005 eV für die Austrittsarbeit und $\pm 1 \cdot 10^{-12}$ Elektronen/Photon · Grad^2 für die Mengenkonstante.

Ergebnisse

Die meisten Filme wurden bei −196 °C aufgedampft, die übrigen bei Zimmertemperatur*). Jeder Film wurde bei einer bestimmten Temperatur T_t 30 Minuten lang getempert, bevor die Chemisorption von CO bei Zimmertemperatur untersucht wurde. In Tabelle 2 sind einige Ergebnisse der an reinen Platinfilmen als Funktion der Aufdampftemperatur T_a und der Sintertemperatur T_t gemessenen Austrittsarbeiten und Mengenkonstanten wiedergegeben. In guter Übereinstimmung mit den von **Suhrmann** und **Wedler** [17] mitgeteilten Resultaten nimmt die Austrittsarbeit der bei −196 °C aufgedampften Filme mit zunehmender Temperatur des anschließenden Temperns zu, diese Abhängigkeit ist in Abb. 2 grafisch dargestellt. Die bei −196 °C gemessenen Werte der Tabelle 2 liegen systematisch einige Hundertstel eV unter dem von **Suhrmann** und **Wedler** gegebenen Wert von 5,48 eV. Die nach dem Tempern auf 20 °C erhaltenen Werte der Austritts-

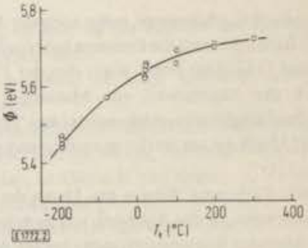


Abb. 2
Austrittsarbeit in Abhängigkeit von der Sintertemperatur

---

*) Für das freundliche Entgegenkommen bei der Eichung sei insbesondere den Herren **Kock**, **Wedler** und **Wölfing** herzlich gedankt.

*) Dabei wurde auf der Photokathode 80 ± 15 °C gemessen.

Tabelle 2
Austrittsarbeit Ø und Mengenkonstante M für Filme verschiedener Aufdampftemperatur (T_a) und Sintertemperatur (T_s)

T_a (°C)	T_s (°C)											
	−196°		−78°		20°		100°		200°		300°	
	Ø	log M	Ø	log M	Ø	log M	Ø	log M	Ø	log M	Ø	log M
−196	5,47	−10,45	–	–	5,65	−10,52	–	–	–	–	–	–
−196	5,46	−10,48	–	–	5,66	−10,65	5,69	−10,53	–	–	–	–
−196	5,44	−10,54	–	–	5,62	−10,64	–	–	5,70	−10,74	–	–
−196	5,45	−10,44	5,57	−10,48	5,62	−10,46	5,66	−10,57	5,71	−10,74	5,72	−10,82
80 ± 15	–	–	–	–	5,71	−10,87	–	–	5,72	−10,97	–	–

arbeit stimmen mit dem von **Suhrmann** und **Wedler** mitgeteilten Ergebnis von 5,63 eV innerhalb der Reproduzierbarkeitsgrenzen überein.

Platin, das ohne äußere Kühlung des Kathodenträgers aufgedampft wurde, wobei in situ eine Temperatur von 80 ± 15 °C gemessen wurde, besitzt eine höhere Austrittsarbeit als ein bei −196 °C aufgedampfter und danach bei 100 °C gesinterter Film. Dieser Befund zeigt, daß das etwa zweistündige Aufdampfen eine weitergehende Ordnung des Filmes ermöglicht als das halbstündige Sintern eines ungeordneten Filmes.

Die Änderung der lichtelektrischen Empfindlichkeit beim langsamen Einströmen von Kohlenmonoxyd in die Photozelle bei Zimmertemperatur ist für Licht von 214 nm und einen verhältnismäßig ungeordneten Film in Abb. 3 gezeigt. Hierbei lassen sich die folgenden Phänomene unterscheiden:

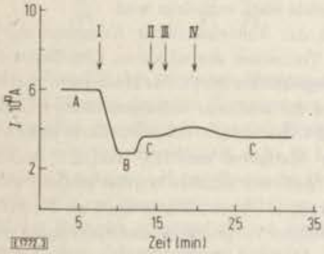


Abb. 3
Photostrom bei kontinuierlicher Zugabe von CO

I. Anfang CO-Zugabe ($p = 10^{-6}$ Torr)
II. Anfang des Druckanstieges nach Erreichen des zweiten, stabilen Wertes (C)
III. $p = 10^{-4}$ Torr
IV. Abpumpen nach Erreichen eines Druckes von 10^{-3} Torr
A. Photostrom des jungfräulichen Films
B. Erster, stabiler Chemisorptionszustand
C. Zweiter, stabiler Chemisorptionszustand

1. Zunächst sinkt der Photostrom vom Anfangswert A des reinen Platins auf einen stabilen Wert B, der auch bei weiter fortgesetztem Einströmen von CO einige Zeit unverändert bleibt. Auch beim Beendigen der CO-Zufuhr und Abpumpen bleibt die lichtelektrische Empfindlichkeit konstant. Das gleiche trifft zu, wenn schon vor Erreichen von B abgepumpt wird.

2. Setzt man die Zugabe von CO weiter fort, läßt sich ein Wiederansteigen des Photostroms beobachten, während der Druck zunächst noch immer den stationären Wert von 10^{-6} Torr besitzt. Danach erreicht der Photostrom einen konstanten Wert C. Bei weiter fortgesetztem Einströmen von CO steigt der Druck an, während der Photostrom vorerst unverändert bleibt. Dieser nimmt jedoch erneut zu, sobald der Druck über 10^{-4} Torr steigt. Beim Abpumpen erweist sich diese Zunahme des Photostromes als reversibel, er sinkt wieder auf den Wert C.

Da die Zustände A, B und C stabil sind, ist es möglich, sie durch vollständige spektrale Verteilungskurven zu charakterisieren. Die hieraus errechneten Werte von Austrittsarbeit und Mengenkonstante sind in Tabelle 3 für Platinfilme verschiedenen Ordnungsgrades zusammengestellt. Es zeigt sich, daß für alle Filme die Adsorption von CO bei Zimmertemperatur anfänglich eine Erhöhung der Austrittsarbeit bewirkt, die jedoch weniger als 0,1 eV beträgt. Für die Filme geringen Ordnungsgrades durchläuft die Austrittsarbeit ein Maximum, um dann wieder abzusinken, so daß die Austrittsarbeit im Zustande C nur wenige Hundertstel eV größer ist als die des jungfräulichen Films. Für die stärker geordneten Filme (bei 80 °C aufgedampft oder bei −196 °C aufgedampft und bei 200 °C gesintert) läßt sich kein Maximum der Austrittsarbeit mehr nachweisen. Bei keinem der von uns untersuchten Filme sank die Austrittsarbeit unter den Anfangswert der jungfräulichen Oberfläche.

Tabelle 3
Austrittsarbeit Ø und Mengenkonstante M für Filme verschiedener Aufdampftemperatur (T_a), Sintertemperatur (T_s), sowie die Chemisorptionszustände B und C

T_a (°C)	T_s (°C)	jungfräulicher Film (A)		CO (B)		CO (C)		ΔØ	
		Ø	log M	Ø	log M	Ø	log M	(B)	(C)
−196	20	5,65	−10,5	5,71	−10,67	5,66	−10,65	+0,06	+0,01
−196	100	5,68	−10,58	5,75	−10,78	5,71	−10,78	+0,07	+0,03
−196	200	5,72	−10,75	5,78	−10,87	5,77	−10,85	+0,06	+0,05
−196	300	5,72	−10,82	5,78	−10,83	5,79	−10,78	+0,06	+0,07
80 ± 15	(20)	5,68	−10,70	5,69	−10,92	5,70	−10,93	+0,01	+0,02
80 ± 15	200	5,72	−10,97	5,78	−10,97	5,78	−10,94	+0,06	+0,06

Die Mengenkonstante wird – mit Ausnahme des am stärksten geordneten Films – durch CO-Zugabe anfänglich erniedrigt. Bei weiterer CO-Zufuhr scheint sie wieder anzusteigen, der Unterschied zwischen Endwert und Minimum liegt jedoch innerhalb der Fehlergrenzen.

Diskussion

Die Versuchsergebnisse legen die folgende Deutung nahe:

1. Kohlenmonoxyd bildet mit Platin bei Zimmertemperatur mindestens zwei unterscheidbare Chemisorptionskomplexe, die zu Austrittsarbeitsänderungen entgegengesetzten Vorzeichens führen. Bei geringem Bedeckungsgrad überwiegt der austrittsarbeitserhöhende Komplex I, der bei Zimmertemperatur nicht abpumpbar ist. Der Komplex II mit umgekehrter Polarität hat wahrscheinlich eine mit zunehmendem Bedeckungsgrad abnehmende Adsorptionswärme, so daß bei Zimmertemperatur ein kleiner Teil des so gebundenen Kohlenmonoxyds abpumpbar ist. (Siehe die geringfügige Abnahme des Photostromes nach dem Abpumpen in Abb. 3. Natürlich ist es formell auch möglich, diese Beobachtung einem dritten, schwach gebundenen, ebenfalls elektropositiven Komplex zuzuschreiben.)

Die Annahme der Existenz von zwei Adsorptionskomplexen entgegengesetzter Polarität ist auch mit den Ergebnissen von Lewis und Gomer [23] im Einklang. Diese Autoren fanden mit Hilfe des FEM (= Feldelektronenmikroskop), daß – neben dem sehr schwach gebundenen physikalisch adsorbierten Kohlenmonoxyd, das schon unterhalb 50°K desorbiert wird – zwei unterscheidbare Chemisorptionskomplexe von Kohlenmonoxyd auf Platin auftreten. Sie stützen sich bei dieser Feststellung auf die beobachtete Zunahme der Austrittsarbeit beim Erwärmen der mit Kohlenmonoxyd bedeckten Pt-Spitze von 50°K auf etwa 300°K. Da hierbei der prae-exponentielle Faktor der Fowler-Nordheim-Charakteristik konstant bleibt, nehmen Lewis und Gomer an, daß bei diesem Erwärmen keine Desorption oder Adsorption auftrete, die Austrittsarbeitszunahme müsse daher einem Umklappen von Chemisorptionskomplexen zugeschrieben werden. Entweder liege bereits bei 50°K ein elektropositiver Komplex neben einem elektronegativen vor und gehe beim Erwärmen der eine in den anderen über, oder das Erwärmen bewirke, daß ein schwach elektronegativer Komplex in einen stärker elektronegativen Komplex umklappe.

2. Die beiden Komplexe verschiedener Polarität werden an Platinproben verschiedener Vorgeschichte in verschiedenen Mengenverhältnissen gebildet. Die Ergebnisse der Tabelle 3 zeigen, daß die Abnahme der Austrittsarbeit nach vorhergehender Zunahme um so geringer ist, je stärker die Filme durch vorheriges Tempern geordnet wurden. Da beim Tempern bekanntlich Gitterfehler und instabile Kristallflächen verschwinden, liegt die Deutung nahe, daß die beiden Komplexe auf verschiedenen Kristallflächen in verschiedener relativer Konzentration auftreten. Dabei dürfte der austrittsarbeitserhöhende Komplex I überwiegend auf den stabilen Kristallflächen, etwa den (111)-Flächen mit dichtester Atompackung auftreten, während der zweite Komplex auf den „rauheren" Kristallflächen vorherrschen sollte, die an der Oberfläche der ungetemperten Filme relativ stärker vertreten sind als an der der geordneten Filme. Hiermit ist der Befund von Eischens [11] insofern im Einklang, als die Existenz zweier Komplexe spektroskopisch nur bei dem auf einem Al_2O_3-Träger dispergierten Platin nachgewiesen wurde. Bekanntlich ist der Durchmesser der Platinpartikeln beim Pt/Al_2O_3-Katalysator wesentlich kleiner als in Platinfilmen, auf Grund dessen weisen die Pt-Kristallflächen im Pt/Al_2O_3-System verhältnismäßig mehr Flächenelemente kleiner Atomdichte auf.

Die Ergebnisse von Lewis und Gomer [23] bieten keine Stütze für die Annahme einer verschiedenen Flächenspezifizität der beiden Chemisorptionskomplexe, da diese Autoren visuell im FEM keine Änderung der Emissionsanisotropie bei der Adsorption von Kohlenmonoxyd oder dem darauffolgenden Aufheizen feststellten. Wir meinen jedoch, daß, solange keine "probe-hole"-Messungen vorliegen [13], der Aussagewert dieser visuellen Wahrnehmungen sehr begrenzt ist. Die Abwesenheit einer Änderung der Emissionsanisotropie im FEM besagt ja gerade, daß die dunklen Flächen auch nach der Adsorption dunkel bleiben und kaum zur Emission beitragen. Das trifft insbesondere für die (111)- und (100)-Flächen zu. Diese gehen folglich nur mit ganz geringem Gewicht in die Fowler-Nordheim-Geraden ein, aus denen Φ_0 und Φ_θ berechnet werden. Das FEM ohne "probe-hole" verschafft daher über die stabilen Kristallflächen, die in den Platinfilmen überwiegen, keine andere Information als die negative Aussage, daß die Austrittsarbeit dieser Flächen durch adsorbiertes Kohlenmonoxyd nicht stark erniedrigt wird.

3. Durch das Auftreten zweier Komplexe mit entgegengesetztem Vorzeichen der effektiven Oberflächendipole und von der Vorgeschichte des Platins abhängiger relativer Häufigkeit werden die scheinbar widersprüchlichen Literaturwerte der Tabelle 1 verständlich. Diese wurden ja nicht nur mit verschiedenen Methoden ermittelt, wodurch prinzipiell verschiedene Meßwerte erhalten werden können, wie schon in der Einleitung erwähnt, sondern auch an Platinoberflächen mit verschiedener Vorgeschichte und daher auch verschiedener Verteilung der Kristallflächen. Demnach erscheinen die von uns untersuchten Filme denen von Heyne und Tompkins [20] besonders ähnlich, was auch auf Grund der experimentellen Bedingungen plausibel ist.

Auch die Ergebnisse von Morgan und Somorjai [22] stehen zu unseren Ergebnissen nicht im Widerspruch. Diese Autoren untersuchten die Chemisorption von CO auf den (100)- und (111)-Flächen von Platin und fanden für diese stabilen Kristallflächen erheblich kleinere $\Delta\Phi$-Werte ($\Delta\Phi_{100} = 0{,}18$ eV; $\Delta\Phi_{111} = 0{,}17$ eV) als bei den FEM-Untersuchungen [21, 23], bei denen diese Flächen praktisch nicht mitgezählt werden.

Da kubisch flächenzentrierte Metalle nach Stranski [24] im Gleichgewicht aus Kubooktaedern bestehen, sollte die Oberfläche von getemperten Platinfilmen überwiegend aus (100)- und (111)-Flächen aufgebaut sein.

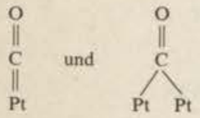
4. Von großem Interesse ist die Frage, wie die verschiedenen Pt–CO-Chemisorptionskomplexe, deren schiere Existenz nun durch verschiedene unabhängige Methoden sichergestellt ist, hinsichtlich der geometrischen Struktur und des quantenmechanischen Bindungscharakters zu definieren sind.

Hierzu sei mit Nachdruck bemerkt, daß die experimentellen Daten, die mit nur einer Methode gemessen wurden, wie etwa die Ergebnisse in dieser Arbeit, keine eindeutige Beschreibung zulassen. Nur bei Berücksichtigung der Gesamtheit des heute vorliegenden Materials über das System Pt – CO und ähnliche Chemisorptionssysteme scheint die Formulierung von Hypothesen gerechtfertigt.

Allgemeine Übereinstimmung besteht darüber, daß chemisorbiertes Kohlenmonoxyd durch eine Pt – C-Bindung an die Oberfläche gebunden ist und nicht durch eine Pt – O-Bindung. Diese Auffassung wird insbesondere durch die Arbeiten von Eischens c.s. [11] und Tucker [25] gestützt.

Innerhalb des hierdurch gegebenen Rahmens sind im Prinzip zwei Hypothesen für die Deutung der verschiedenen Pt – CO-Komplexe möglich.

Hypothese I geht von dem – meist stillschweigenden – Postulat aus, daß auch bei vollständiger Bedeckung alle Platinatome der Oberfläche auf ihren ursprünglichen Gitterplätzen verbleiben. Die Existenz verschiedener Chemisorptionskomplexe auf ein und derselben Kristallfläche muß dann einem verschiedenartigen Bindungscharakter der Komplexe zugeschrieben werden. Naheliegend ist dabei die Annahme von linearen und brückenförmigen Komplexen:



Da es jedoch schwerfällt, bei gegebenen Elektronegativitäten von Pt und CO für zwei derartige Komplexe ein entgegengesetztes Vorzeichen des effektiven Pt – CO-Bindungsdipols anzunehmen, ist es vollkommen logisch, daß z. B. Lewis und Gomer, die ihre Ergebnisse auf dem Boden der Hypothese I interpretieren, lieber von einem stärker und einem schwächer elektronegativen Komplex sprechen als von einem elektropositiven neben einem elektronegativen Komplex.

Hypothese II verläßt das beschränkende Postulat der Hypothese I, läßt also zu, daß Pt-Atome der Oberfläche bei hoher Bedeckung ihre ursprünglichen Gitterplätze verlassen und sich auf energetisch günstigere Plätze zwischen bzw. über den adsorbierten Atomen begeben. Die energetische Triebfeder für diese „korrosive Chemisorption" ist die gleiche wie die bei der Bildung etwa eines Oxydes oder eines Carbonyls, wobei Metallatome ebenfalls ihre Gitterplätze verlassen. Die Aktivierungsenergie für diese Umgruppierung wird durch die Adsorption stark herabgesetzt, da die Bildung neuer stark lokalisierter chemischer Bindungen zwischen einem Pt-Atom und einem CO-Molekül die ursprünglichen Bindungen zwischen dem Pt-Atom und seinen Nachbarn im Metallgitter stark in Mitleidenschaft zieht.

Die Hypothese II, wonach neben der „Chemi-Adsorption" (ohne Umgruppierung der Metallatome) auch „korrosive Chemisorption" auftreten kann, beschränkt im übrigen nicht die schon bei Hypothese I genannten Möglichkeiten, daß z. B. lineare und brückenförmige Komplexe nebeneinander coexistieren können.

Die Frage ist nun, ob die beiden Chemisorptionskomplexe des Pt – CO-Systems auf der Grundlage der Hypothese I oder der Hypothese II zu deuten sind. Eine Entscheidung darüber erlauben weder photoelektrische noch FEM-Messungen. Lediglich die Feldionenmikroskopie gestattet eindeutige Aussagen darüber, ob Metallatome der Oberfläche bei der Chemisorption eines Gases ihre Plätze verlassen oder nicht. Manchmal geben auch LEED-Ergebnisse wertvolle Hinweise, doch oft lassen sich die mit LEED gefundenen Strukturen mit beiden Hypothesen deuten.

Feldionenmikroskopische Bilder von Platinoberflächen nach Adsorption von Kohlenmonoxyd bei Zimmertemperatur liegen im Augenblick leider nicht vor. Dagegen ist das analoge System W – CO [18], ebenso wie W – N_2 [19] sehr eingehend mit Hilfe des Feldionenmikroskopes untersucht worden. Für Wolfram fanden Holscher und Sachtler [18], daß Adsorption von CO bei Zimmertemperatur eine äußerst intensive Umgruppierung der oberflächennahen W-Atome mit sich bringt. Durch Feldverdampfung konnte nachgewiesen werden, daß sogar die Atome unmittelbar unterhalb der Oberfläche mit „umgepflügt" wurden. Unsere Deutung der Feldionenbilder des Systems W – CO im Sinne einer korrosiven Chemisorption stieß zwar im Anfang auf Skepsis bei Ehrlich [26], doch in der Folgezeit konnte diese Deutung durch Holscher [27] weiter untermauert werden, und E. W. Müller [28] teilte mit, daß er auf Grund anderer feldionenmikroskopischer Untersuchungen zu dem gleichen Schluß gelangt war.

Da die Sublimationswärme des Platins erheblich geringer ist als die des Wolframs, während die Adsorptionswärme von CO an Pt mit 32 kcal/mol [21, 23] recht erheblich ist, sind wir der Ansicht, daß auch für das System Pt – CO eine Deutung im Sinne der Hypothese II gerechtfertigt ist. Dabei sei daran erinnert, daß der gemessene Wert von $\Delta \Phi$ nicht durch den Pt – CO-Bindungsdipol an sich, sondern durch dessen Komponente in Richtung der Oberflächennormalen gegeben ist. Bei korrosiver Chemisorption kann sich daher auch bei konstantem Bindungsdipol das Vorzeichen von $\Delta \Phi$ umdrehen, wenn nämlich das Platinatom nach außen springt, so daß man diesen Dipol „von hinten" sieht. Wir nehmen daher vorläufig an, daß der Komplex I als Chemi-Adsorption, der Komplex II als korrosive Chemisorption aufzufassen ist.

Für das System W – CO konnte gezeigt werden, daß die korrosive Chemisorption zuerst an den rauhen Kristallflächen einsetzt, während an den glatten, stabilen Kristallflächen die Chemi-Adsorption noch überwiegt. Wir sehen in dieser Übereinstimmung der Ergebnisse hinsichtlich der Austrittsarbeitsänderungen bei W – CO und Pt – CO eine unabhängige Stütze für den oben ausgesprochenen Schluß, daß der Chemisorptionskomplex II insbesondere auf „rauhen" Kristallflächen gebildet wird, ohne allerdings ausschließlich auf diese beschränkt zu sein.

Die Untersuchungen wurden unterstützt von der Niederländischen Stiftung für Chemische Forschung (S.O.N.) mit einer Subvention der Niederländischen Organisation für reinwissenschaftliche Forschung (Z.W.O.).

Wir danken Herrn F. C. Kauffeld für die sinnreiche Entwicklung und den Bau der Photozelle.

Literatur

[1] R. Suhrmann, Adv. Catalysis VII (1955).

[2] R. Suhrmann, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *60*, 804 (1956).

[3] R. Suhrmann und G. Wedler, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *63*, 748 (1959).

[4] W. M. H. Sachtler und G. J. H. Dorgelo, Z. physik. Chem. NF *25*, 69 (1960).

[5] F. Bloyaert, L. D'Or und J. C. P. Mignolet, J. Chim. physique *54*, 53 (1957).

[6] R. V. Culver, J. Pritchard und F. C. Tompkins, Z. Elektrochem., Ber. Bunsenges. physik. Chem. *63*, 741 (1959).

[7] R. V. Culver und F. C. Tompkins, Adv. Catalysis XI (1959).

[8] A. Eberhagen, Fortschr. Physik *8*, 245 (1960).

[9] R. Suhrmann, H. Ober und G. Wedler, Z. physik. Chem. NF *29*, 305 (1961).

[10] W. M. H. Sachtler, C. R. Kiliszek und B. E. Nieuwenhuys, Thin Solid Films 2, 43 (1968).

[11] R. P. Eischens und W. A. Pliskin, Adv. Catalysis X (1958).

[12] A. A. Holscher, Surface Sci. *4*, 89 (1966).

[13] W. M. H. Sachtler, Angew. Chem. *7*, 668 (1968).

[14] G. Ehrlich, Adv. Catalysis *14*, 255 (1963).

[15] G. J. H. Dorgelo und W. M. H. Sachtler, Naturwissenschaften *46*, 576 (1959).

[16] L. A. Rudnitskii, L. I. Tjachovskai, N. V. Kulkova und T. I. Temkin, C. R. [Doklady] Acad. Sci. SSSR *182*, 1358 (1968).

[17] R. Suhrmann und G. Wedler, Z. angew. Physik *14*, 70 (1962).

[18] A. A. Holscher und W. M. H. Sachtler, Discuss. Faraday Soc. *41*, 29 (1966).

[19] A. A. Holscher und W. M. H. Sachtler, Molecular Processes on Solid Surfaces. Herausg. von E. Drauglis, R. D. Gretz und R. I. Jaffee, McGraw-Hill, New York (1969) 317.

[20] H. Heyne und F. C. Tompkins, Proc. Roy. Soc. [London] Ser A *292*, 460 (1966).

[21] W. J. M. Rootsaert, L. L. van Reyen und W. M. H. Sachtler, J. Catalysis *1*, 416 (1962).

[22] A. E. Morgan und G. A. Somorjai, J. chem. Physics *51*, 3309 (1969).

[23] R. Lewis und R. Gomer, Suppl. Nuovo Cimento *V*, 2, 506 (1967).

[24] I. N. Stranski und R. Kaischew, Z. physik. Chem. *B 26*, 312 (1934).

[25] C. W. Tucker, Surface Sci. 2, 516 (1964).

[26] G. Ehrlich, Discuss. Faraday Soc. *41*, 54 (1966).

[27] A. A. Holscher, "Adsorption Studies with the Field-Emission and Field-Ion Microscope", Dissertation, Leiden, Niederlande, 1967.

[28] E. W. Müller, Molecular Processes on Solid Surfaces. Herausg. von E. Drauglis, R. D. Gretz und R. I. Jaffee. McGraw-Hill, New York (1969) 67.

E 1772

Chapter IV

IV.1. PHOTOELECTRIC DETERMINATION OF THE WORK FUNCTION OF Ru-FILMS AS A FUNCTION OF SINTERING TEMPERATURE (78°K - 925°K)*

by

R. Bouwman and W.M.H. Sachtler

Afdeling Heterogene Katalyse
Chemische Laboratoria, Rijksuniversiteit, Leiden
the Netherlands

Summary

The photoelectric work function Φ and the emission constant M of clean ruthenium films evaporated on pyrex substrates at 78°K and on non-cooled, highly outgassed quartz substrates were determined after sintering at various temperatures up to 1,000°K.
For films deposited on pyrex substrates and subsequently sintered Φ rises from 4.52 ± 0.03 eV at 78°K to 5.02 ± 0.03 eV at 573°K. For films evaporated on quartz an annealed above 700°K, Φ is 5.10 ± 0.05 eV.
The emission constant M continues to decrease even beyond the temperature where Φ ceases to increase.
On the basis of their position in Group VIII the work function of Rh and Os films deposited at 78°K and sintered at 373°K are predicted to be 5.1 - 5.2 eV and 4.9 - 5.0 eV respectively.

---

* Surface Science, in press.

1. Introduction

Interest in the chemical and physical properties of ruthenium surfaces has increased in recent years for a variety of reasons including the extraordinary catalytic and electrochemical qualities of certain ruthenium alloys[1-3]. Data on the electronic parameters characterizing the surface of clean ruthenium are, however, extremely scarce, since methods to prepare reliably clean ruthenium surfaces have become available only recently. The few results reported in the last few years on the work function of ruthenium[4-5] are, moreover, conflicting, while data on the photoelectric emission of ruthenium seem to be lacking completely. For an understanding of the peculiar behaviour of ruthenium in catalysis, electrochemistry and other branches of surface science one may assume that photoelectric data on the work function will be of greater value than thermionic data because the latter method can only provide information on highly sintered surfaces, while the photoelectric method is capable of evaluating the work function of vapour deposited metal surfaces in their virgin state and in any state of annealing. Recent results[6-8] have shown that it is insufficient to characterize the work function of a metal film by a single value since the work function change with annealing temperature is not only very remarkable but also a valuable source of information on the reconstruction of a surface leading to disappearance of lattice imperfections and high index crystal faces during sintering.

In this paper results are presented on the photoelectric emission of clean ruthenium films, prepared by deposition from the vapour in ultrahigh vacuum followed by annealing under carefully controlled conditions. As this study is part of a program to investigate the work functions of Group VIII metals and their alloys we shall also discuss the systematic trends in the work function data of the nine metals in Group VIII on the basis of the data available at present.

2) Experimental

The photoelectric measurements were carried out by directing a light beam produced by a Bausch & Lomb grating monochromator equipped with a high pressure mercury lamp either to a calibrated phototube containing a tantalum film as photocathode or to the phototube containing a ruthenium film as photocathode. Photocurrents from both tubes were measured by an E.I.L. vibrating reed electrometer type 51A, capable of reproducing photocurrents down to 10^{-14} Amp.

Two types of phototubes were used. For the majority of the experiments where annealing of the ruthenium film took place at temperatures not exceeding 600°K, the tube shown in Fig. 1 and described in ref. 7 (tube I) was used. A second phototube[9] (tube II) was specially designed for experiments where ruthenium films were to be annealed at temperatures above 700°K. In tube II the cathode support consisted of quartz. No forced cooling took place during deposition of the film, but subsequent sintering was effected by

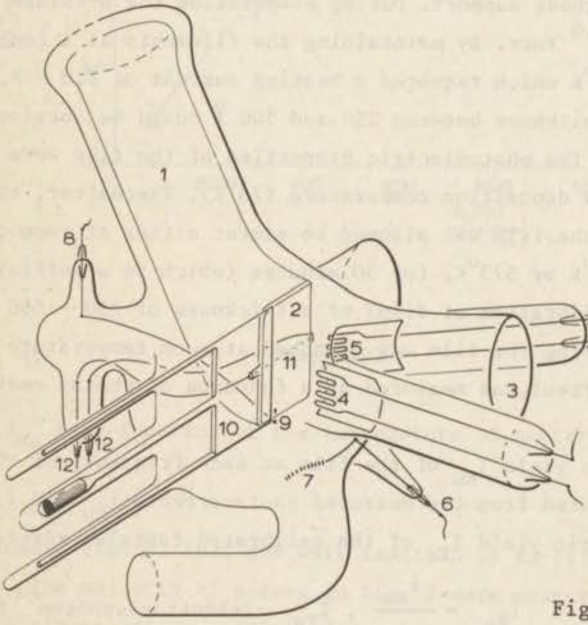


Figure 1

Phototube I.

heating a resistance wire fused in the backside of the quartz plate. Annealing temperatures up to 1,000°K could be achieved with this tube without impairing the vacuum.

The usual procedure was as follows.

Spec pure Ru-pellets* having a diameter of 0.1 - 0.2 mm were spot-welded to a multi-hair-pin tungsten filament having a diameter of 0.3 mm, the latter being used as evaporation source.

After reduction of the ruthenium sources in hydrogen, the apparatus was evacuated. Only after having obtained a steady state pressure below 5.10^{-10} Torr and after thorough outgassing of the ruthenium sources which was accompanied by preevaporation of roughly 10% of the available ruthenium, while shielding the cathode support, the metal was evaporated on the cooled cathode support. During evaporation the pressure did not rise above 5.10^{-10} Torr. By maintaining the filaments at a temperature of 2,225 - 2,275°K which required a heating current of 8.0 - 8.5 Amp, films having a thickness between 250 and 500 Å could be obtained within about two hours. The photoelectric properties of the film were first determined at the deposition temperature (78°K). Thereafter, the coolant was removed and the film was allowed to sinter either at room temperature, or at 373°K, 473°K or 573°K, for 30 minutes (which is a sufficient period of time for equilibration of films of a thickness of 250 - 500 Å [10-11]). After this sintering the film was quenched at room temperature and the photoelectric current was measured as a function of photon energy.

The photoelectric yield I_{Ru} of the film at each frequency of the incident light was calculated from the measured photocurrents i_{Ru} and i_{Ta} and the known photoelectric yield I_{Ta} of the calibrated tantalum reference tube according to

$$I_{Ru} = \frac{i_{Ru}}{i_{Ta}} \cdot I_{Ta} \quad (\text{electrons.photon}^{-1})$$

By plotting $\sqrt{I_{Ru}}$ against the energy E of the light a linearized Fowler plot[12] is obtained from which the work function Φ of the film can be calculated from the intercept on the abscissa and the emission constant M from the slope.

---

* The Ru-pellets were obtained by melting Ru-sponge (Johnson, Matthey & Co., London) in an argon arc.

3. Results

The results on fifteen different Ru-films prepared under identical conditions are shown in Fig. 2. The linearized Fowler plots for some Ru-films are shown in Fig. 3.

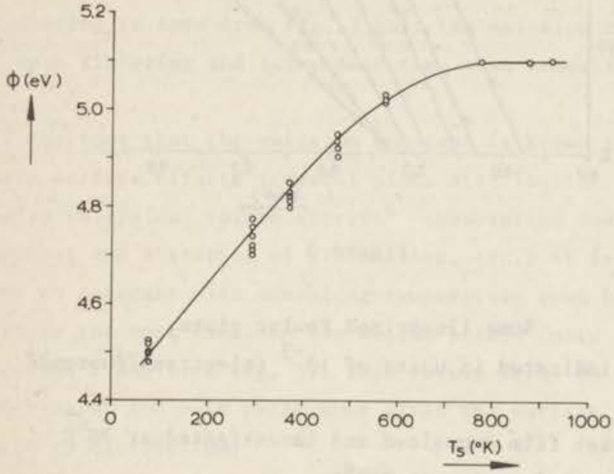


Figure 2

Φ_{Ru} as a function of the temperature of sintering T_s.

It is evident (Fig. 2) that the work function of Ru-films increases by sintering. The majority of points in Fig. 2 were measured with phototube I and the remaining points corresponding to annealing temperatures above 750°K were obtained in tube II with Ru-films deposited on quartz and sintered at 773°K or 925°K. These films which were evaporated on a non-cooled, polished quartz support whereby in-situ deposition temperatures of 375° - 525°K were measured, possess initially a higher work function ($\phi \cong 5.0$ eV) than films evaporated at 78°K and sintered at 375° - 525°K during 30 minutes. In this respect ruthenium confirms our experiments

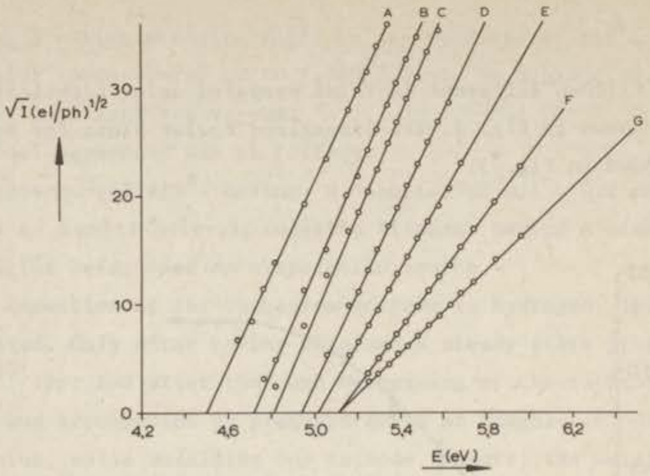


Figure 3

Some linearized Fowler plots.

$\sqrt{I}$ is indicated in units of 10^{-3} (electrons/photon)$^{\frac{1}{2}}$

A = Fresh film deposited and investigated at 78°K
B = After sintering at 295°K
C = After sintering at 373°K
D = After sintering at 473°K
E = After sintering at 573°K
F = After sintering at 673°K
G = After sintering at 925°K

with other metals[7], in that deposition at a certain in-situ temperature T_s leads to a higher work function than deposition on a substrate cooled by liquid nitrogen followed by sintering at the same temperature T_s. It has also been found by other authors[10] that substantial in-situ ordering is effected when the substrate temperature is high. After sintering at a much higher temperature the differences due to the different deposition temperatures disappear. We, therefore, feel that we may justifiably include in Fig. 2 the results measured in phototube II after annealing at temperatures above 750°K. The line drawn through the totality of measured points then reflects our assumption that the differences in deposition temperature and the differences in cathode substrate (borosilicate glass or quartz) are of no relevance for the work function of the annealed films.

It is interesting to note from Fig. 3 that the emission constant M first increases upon sintering and later decreases when annealing is more rigorous.
In view of the fact that the emission constant is known to depend not only on mere surface effects (crystal plane distribution, roughness factor) but also on typical volume effects[8] (absorption coefficient for photons, number and character of dislocation, etc.) it is noteworthy that M continues to decrease with annealing temperature even beyond the temperature where the work function has become stable (note the different slope of curves F and G in Fig. 3). This result seems to indicate continued ordering of the bulk phase even after the surface structure has been brought to equilibrium.

4. Discussion

The present results for the work function of ruthenium films can be compared with the work function ($\Phi = 4.55 \pm 0.05$ eV) reported by Psarouthakis and Huntington[5] and to the values quoted by Rivière[4] from unpublished work for ruthenium films on tungsten ($\Phi = 4.865 \pm 0.005$ eV) and for polycrystalline foils ($\Phi = 4.730 \pm 0.010$ eV).
These literature data were obtained by the thermionic emission method. Another value obtained in 1938 by Klein and Lange[13] from contact potential measurements ($\Phi = 4.52$ eV) is of mere historic interest in view of the inadequate vacuum technique used.
When comparing results on films and thermionic emitters it seems logical to expect best agreement for films annealed at the highest temperatures. However, in thermionic emitters, i.e. filaments or foils heated to incandescence for prolonged periods, traces of metallic impurities having

a low surface energy will diffuse outward and become concentrated in the surface layers even if their concentration is in the p.p.m. range. In view of the considerable difference between our annealed films ($\Phi = 5.10 \pm 0.05$ eV) and the thermionic emitters ($\Phi = 4.55 \pm 0.05$ eV) it is interesting to compare for other metals the values obtained by photoemission of films and by thermionic emission respectively. In Table I literature values for Group VIII elements and other refractory metals are shown.

TABLE I

A comparison between data of work functions of thermionic emitters and of films

Metal	Work function (eV) of thermionic emitters.	Ref.	Photoelectric work function (eV) of films.	Ref.
Fe	4.34; 4.5	14,17,18	4.71 (373°K); 4.72 (373°K)	6
Co	4.4	18,19	4.97 (373°K)	6
Ni	4.41; 4.6	14,17,18,19	5.25 - 5.28 (423°K) 5.05 - 5.20 (373°K) 4.87 - 4.95 (293°K)	6 6 6
Ru	4.55 ± 0.05	5	5.10 ± 0.05 (925°K) 4.83 ± 0.03 (373°K) }	this paper
Rh	4.8	18,19		
Pd	4.9; 4.8; 4,99	18,20,19	5.40 (388°K)	22
Os	4.7; 4.83	18,21		
Ir	5.3; 5.27; 5.4	18,21,19	5.35 (373°K)	23
Pt	5.3; 5.79 ± 0.09	18,19,14	5.63 (295°K); >6.2 5.72 (573°K) 5.68 (373°K)	6,15 7 7
W	4.5; 4.52; 4.54	18,21,19	4.63 (438°K); 4.55 (403°K)	6,22
Ta	4.1; 4.52 ± 0.05	18,19,21	4.12 *)	24
Mo	4.2; 4.03 - 4.12	18,21	4.35 *)	15

*) The values of Ta- and Mo- films were obtained from films evaporated on non-cooled supports.

It is interesting to note that in the majority of cases, the work function of annealed films derived from photoelectric data are higher (as much as 0.5 eV) than the work function obtained from thermionic emission. Even more striking is the conclusion that in those cases when the reported data seem to agree numerically for the two methods, it is almost certain that the films were not appropriately annealed. Elsewhere it is shown[25] that an annealing temperature T_s of one-third of the melting temperature T_m is required to obtain sufficient equilibration so that further sintering does not cause a further increase in work function. For tungsten e.g. this leads to the requirement $T_s \cong 1{,}250^{\circ}K$. Only in the case of platinum is there good agreement between recent results of the thermionic work function[14] and photoelectric values obtained on films by Suhrman and Wedler[6] and ourselves[7]. (The Pt-value of 6.2 eV quoted by Herring and Nichols[15] is most probably representative for an oxygen-contaminated sample.)

Several authors have tried to predict work function by assuming specific physical relationships with other physical properties (e.g. as a function of the ionization potential[16]). Predictions based on quantum-mechanical calculations are not yet possible.
There seems, however, to be unanimity on the view that the work function is characteristic for the position of the element in the periodic table. The similarities of the work functions of for instance Na and K or Mo and W are usually considered as being in line with the resemblances in the chemical properties of two elements in the same column of the periodic table of the elements. As the work function also depends on the structure of the surface, a comparison is most meaningful if metals of equal crystal structure and in the same group of the periodic table are compared. In this respect the elements of the VIIIth group are almost ideal. With the exception of iron they all belong to either the f.c.c. or the h.c.p. structure. These two structures have much in common especially the packing density of the most stable crystal plane prevailing in the surface. For this group of metals it should therefore be possible to predict by simple interpolation the work functions of those elements for which at present no data are available.
Using recent reliable data on the photoelectric work function of metal films prepared and sintered under identical conditions* including the

---

* We have chosen a deposition temperature of $78^{\circ}K$ and an annealing temperature of $373^{\circ}K$, because most data in the literature (Table I) were obtained under these conditions.

Ru value of the present work, the following picture emerges. The work function always rises from left to right in each horizontal triad of Group VIII and from the lighter to the heavier metals in each vertical triad (see Table II).

TABLE II

A comparison of the work functions of Group VIII metal films deposited at 78°K and sintered at 373°K

Fe (4.71)	Co (4.97)	Ni (5.05-5.20)
Ru (4.83)	Rh (--)	Pd (5.40)
Os (--)	Ir (5.35)	Pt (5.68)

No measured values are available for Os and Rh but the availability of a value for Ru now provides us with at least two numbers for each of the three horizontal and the three vertical triads. Only one horizontal (Fe-Co-Ni) and one vertical (Ni-Pd-Pt) triad are completed. It appears that the difference between Φ_{Ni} and Φ_{Pd} is about the same as that between Φ_{Pd} and Φ_{Pt}. Assuming now that the same regularity holds for the two other vertical triads, we arrive at a value for Os of 4.9 - 5.0 eV and for Rh of 5.1 - 5.2 eV for films prepared under the same conditions described above.

The estimated results of this "vertical interpolation" is in fair agreement with that of the "horizontal interpolation". If we insert the values of Os and Rh, we observe that the difference between the first two metals in each horizontal triad is always greater than that between the last two metals. Moreover, the overall difference in each triad increases from the lighter metals to the heavier metals.

5. Acknowledgements

The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

The authors are indebted to Mr. F.C. Kauffeld for skilfully developing and constructing the phototubes and to Drs. H.P. van Keulen and Mr. G.J.M. Lippits for their assistance during the measurements and evaluation of the experimental results.

References

1) D.W. McKee and F.J. Norton, J. Phys. Chem. 68 (1964) 481.

2) G.C. Bond and D.E. Webster, Plat. met. rev. 13 (1969) 57.

3) D.V. Sokol'skii, K.K. Dzhardamalieva, A.G. Sarmuzina and T. Tonmanov, Dokl. Akad. Nauk. S.S.S.R. 176 (1967) 1093.

D.V. Sokol'skii, A.G. Sarmuzina and K.K. Dzhardamalieva, Tr. Inst. Khim. Nauk., Akad. Nauk. Kazakh. S.S.S.R. 17 (1967) 100.

4) J.C. Rivière, The Solid State Surface Science (Dekker, New York, 1969) p. 250.

5) J. Psarouthakis and R.D. Huntington, Surface Sci. 7 (1967) 279.

6) R. Suhrmann and G. Wedler, Z. angew. Phys. 14 (1962) 70.

7) R. Bouwman, H.P. van Keulen and W.M.H. Sachtler, Ber. Bunsenges. physik. Chem. 74 (1970) 198.

8) Th.G.J. van Oirschot, Thesis, Leyden University (1970) the Netherlands.

9) R. Bouwman and F.C. Kauffeld, to be published.

10) J.R. Anderson, General Electric Report 69-C-050 (1969).

11) J.R. Anderson, B.H. Conkey, Proc. I.R.E.E. Australia (1967) 132.

12) W.M.H. Sachtler, G.J.H. Dorgelo and A.A. Holscher, Surface Sci. 5 (1966) 221.

13) O. Klein and E. Lange, Z. Elektrochem. 8 (1938) 542.

14) R.G. Wilson, J. appl. Phys. 37 (1966) 2261.

15) C. Herring, M.H. Nichols, Rev. Mod. Physics 21 (1949) 185.

16) W.M.H. Sachtler, Z. Elektrochem. 59 (1955) 119.

17) H. Moesta, Chemisorption und Ionisation in Metall-Metall Systemen, Springer Verlag, Berlin (1968).

18) D.A. Wright, Radio Section (1952) Paper 1404.

19) "Metals Reference Book" (C.J. Smithells) 3rd ed. Butterworth, London 1962.

20) V.S. Fomenko, Handbook of Thermionic Properties, Plenum Press, New York.

21) R.G. Wilson, J. appl. Phys. 37 (1966) 3170.

22) R. Suhrmann, H. Ober and G. Wedler, Z. phys. Chem. N.F. 29 (1961) 305.

23) R. Bouwman, unpublished.

24) W.M.H. Sachtler, G.J.H. Dorgelo, J. Chem. Phys. 54 (1957) 27.

25) R. Bouwman and W.M.H. Sachtler, Surface Science, in press.

IV.2. PHOTOELECTRIC DETERMINATION OF THE EQUILIBRATION OF METAL AND ALLOY FILMS*

1. Introduction

Metal and alloy films prepared by evaporation under ultrahigh vacuum conditions are objects of research[1-2] on catalysis, adsorption and other topics of surface science and are considered as typical in providing the ideal metal surface of high cleanliness.
However, the advantage of an extremely low contamination level is to some extent counterbalanced by a poor crystallographic definition of the surface of the films. Freshly deposited films deviate from the ideal metal since they are not in true equilibrium. For this reason it is very difficult to compare experimental results of different authors in particular when sintering conditions are not specified precisely.

The departure from equilibrium is responsible for the irreversible changes of certain physical properties of films during annealing. These include the electrical conductivity, the surface area, the line width of X-ray diffraction patterns and others[3].

Of particular interest for surface science is the electronic work function which, generally, increases during annealing of films[4]. Numerical values of the work function are, therefore, meaningful only if the state of annealing of the films is properly defined[5]. Some apparent discrepancies in work function values reported by different authors, e.g. reflect mainly the different temperatures to which the films have been exposed. During annealing, imperfections in the exposed crystal planes disappear

---

* Surface Science, Letter to the Editor, in press.

and closely packed stable crystal planes grow at the expense of less stable faces. Work function changes during annealing of films provide an interesting and rather specific method to study the surface reconstructions. To our knowledge, no systematic investigation exists at present with respect to the problem at what temperatures these surface changes become observable, how the annealing process depends on the nature of the metal, and at which temperature annealing is completed in the sense that further temperature increase has no effect on the work function. Only one qualitative statement appears obvious, viz. that metals of higher melting point and higher heat of sublimation will require higher annealing temperatures.

Because the work function is a property of the surface we have decided to study work function changes during annealing of films in order to get some systematic information on surface reconstruction. Metals with widely differing melting points were selected. The photoelectric technique was chosen to determine the work functions. The films were prepared by vapour quenching on substrates cooled by liquid nitrogen* and they were subsequently heated at various temperatures in specific phototubes described elsewhere[5-6].

2. Results

In Fig. 1 the work functions of gold, platinum and ruthenium films having a thickness of 250 - 500 Å are plotted against the reduced temperature of sintering T_s/T_m (T_s being the true temperature of sintering and T_m the melting point of the metal both expressed in ^{o}K). Evidently, the work function of each metal increases upon annealing and even most drastically below room temperature. The equilibrium value for each metal is obtained at $T_s \cong 0.3\ T_m$. The same value was found for silver and palladium. The result is apparently of general validity and is in agreement with the fact that surface diffusion becomes appreciable

---

* Due to the heat of radiation emitted by the evaporation sources, the temperatures of deposition were slightly higher than 78^{o}K. For Ru for instance, which generates the largest amount of heat, the temperature on the substrate rose to about 85^{o}K.

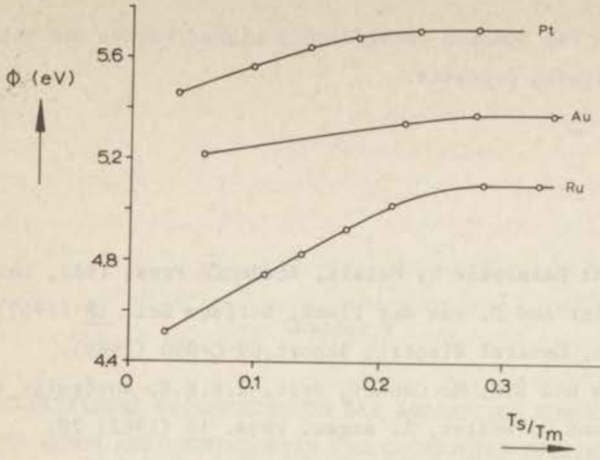


Figure 1

The work function (Φ) of gold, platinum and ruthenium films as a function of the reduced temperature of sintering (T_s/T_m).

at about 0.3 T_m[7], the Tammann temperature. The results are also in line with our previous experience concerning the interdiffusion of binary metal films. For films prepared by vapour quenching of the systems Cu-Ni[8], Au-Pt[9] and Pt-Ru[10] we had found that the equilibrium alloy phases, predicted by thermodynamics are formed within several hours at sintering temperatures lying in between the Tammann temperatures of the two components. Also in this equilibration process surface and grain boundary diffusion are predominant.

Our result that the work function of metal films increases strongly upon sintering up to $T_s \cong 0.3\ T_m$ casts serious doubts[5] on some of the work function data quoted in the literature for refractory metals. In particular the value of 4.5 eV for tungsten used as absolute standard in numerous F.E.M. determinations of work functions appears suspect, as this value was determined on insufficiently sintered films and on filaments heated to incandescence which are known for their tendency to enrich electropositive impurities on their surfaces. Indeed in a recent communication by Van Someren considerably higher values are reported for sublimed tungsten deposits.

References

1) G.C. Bond, in: Catalysis by Metals, Academic Press 1962, London.
2) W.M.H. Sachtler and P. van der Plank, Surface Sci. 18 (1969) 62.
3) J.R. Anderson, General Electric Report 69-C-050 (1969).
J.R. Anderson and B.H. Mc Conkey, Proc. I.R.E.E. Australia (1967) 132.
4) R. Suhrmann and G. Wedler, Z. angew. Phys. 14 (1962) 70.
5) R. Bouwman and W.M.H. Sachtler, Surface Sci. in press.
6) R. Bouwman, H.P. van Keulen,and W.M.H. Sachtler, Ber. Bunsenges. physik. Chemie 74 (1970) 198.
7) S.J. Gregg, in: The Surface Chemistry of Solids, Chapman & Hall Ltd. 1961, London.
8) W.M.H. Sachtler and G.J.H. Dorgelo, J. Catalysis 4 (1965) 654.
W.M.H. Sachtler and R. Jongepier, J. Catalysis 4 (1965) 665.
9) R. Bouwman and W.M.H. Sachtler, J. Catalysis, in press.
10) R. Bouwman and W.M.H. Sachtler, unpublished.
11) L. van Someren, Surface Sci. 20 (1970) 221.

R. Bouwman and W.M.H. Sachtler
Afdeling Heterogene Katalyse
Chemische Laboratoria, Rijksuniversiteit, Leiden
The Netherlands

Chapter V

PHOTOELEKTRISCHE UNTERSUCHUNGEN DER ADSORPTION VON KOHLENMONOXYD UND XENON AUF UNGEORDNETEN UND GEORDNETEN RUTHENIUMFILMEN*

von
R. Bouwman und W.M.H. Sachtler
Afdeling Heterogene Katalyse
Gorlaeus Laboratoria, Rijksuniversiteit, Leiden
Niederlande

Zusammenfassung

Rutheniumfilme werden durch Aufdampfen des spektroskopisch reinen Metalls unter Ultrahochvakuum auf Pyrex- bzw. Quarzträger hergestellt. Die Emission von Photoelektronen dieser Filme wird in Abhängigkeit von sowohl der Tempertemperatur T_t als auch der Belegung mit Kohlenmonoxyd oder Xenon untersucht. Die Austrittsarbeit des reinen Ru steigt erheblich mit T_t von 4,52 eV ($T_t = 78^oK$) bis auf 5,10 eV ($T_t \cong 800^oK$). Nach Chemisorption von CO bei 78°K bzw. 293°K erreichen Austrittsarbeit und Mengenkonstante die gleichen Endwerte für Filme mit verschiedenen Anfangswerten dieser Grössen. Im Gegensatz zu CO bewirkt die Adsorption von Xenon eine praktisch konstante Abnahme von Φ für alle Filme.

Zur Deutung dieser Befunde wird angenommen, dass die bei der Chemisorption von CO freiwerdende Adsorptionswärme ein lokales Tempern anfänglich ungeordneter Ru-Filme bewirkt.

---

* Submitted for publication to "Berichte der Bunsen-Gesellschaft für physikalische Chemie (früher Zeitschrift für Elektrochemie).

Summary

Ruthenium films are prepared under ultra-high vacuum by subliming the spec-pure metal on a pyrex or quartz support. The emission of photoelectrons from these films is studied as a function of the sintering temperature T_t and the coverage with carbon monoxide or xenon. The work function of pure Ru increases considerably with T_t (4.52 eV at $78^\circ K$, 5.10 eV at $\sim 800^\circ K$). After chemisorption of CO at $78^\circ K$ or $293^\circ K$ on films with initially different work functions and emission constants these parameters attain equal finite values.

Quite differently, the adsorption of Xe causes a constant decrease of Φ for all films.

These results are interpreted by assuming that the heat liberated in the chemisorption of CO causes a local sintering of initially imperfect Ru films.

1. Einleitung

Die Oberflächeneigenschaften des Rutheniums sind noch wenig untersucht, da dies Metall erst seit verhältnismässig kurzer Zeit in genügend reiner und für die Herstellung von aufgedampften Filmen geeigneter Form zur Verfügung steht. Vom Standpunkt der heterogenen Katalyse aus gesehen, gehört Ruthenium indessen zu den interessantesten Elementen, da sich in neuerer Zeit die Messdaten häufen, aus denen hervorgeht, dass Platin-Ruthenium-Legierungen als Hydrierungskatalysatoren alle anderen bekannten Stoffe übertreffen [1-2]. Die Tatsache, dass ein Rutheniumzuschlag zum Platin dessen Hydrierungsaktivität bedeutend erhöht, obwohl reines Ruthenium eine wesentlich geringere katalytische Aktivität besitzt als reines Platin, gehört zu den bisher unerklärten Tatsachen der heterogenen Katalyse und stellt darum eine Herausforderung der Grundlagenforschung auf diesem Gebiete dar.

Nachdem sich in letzter Zeit die Beweise häufen, dass die Oberfläche einer Legierung oft eine andere atomare Zusammensetzung besitzt als deren Inneres [3-6], erscheint es erforderlich, für die genannten Platin-Ruthenium-Legierungen sowohl die Oberflächenzusammenstellung im Gleichgewicht als auch die "elektronischen Eigenschaften" dieser Oberfläche, gekennzeichnet durch ihre Chemisorption und Elektronenemission, messend zu erforschen.

Eine Methode, die sich in der jüngsten Vergangenheit zur Kennzeichnung der Oberflächenzusammensetzung von Legierungen als nützlich erwies, ist die chemisorptive Titration [3]. So kann man etwa die Nickelatome in der Oberfläche einer Cu-Ni-Legierung dadurch abzählen, dass man die Wasserstoffadsorption unter Bedingungen misst, bei denen zu erwarten ist, dass jedes in der Oberfläche liegende Nickelatom ein Wasserstoffatom adsorbiert, die Kupferatome dagegen nicht. Will man eine derartige Methode auf Platin-Ruthenium-Legierungen anwenden, muss man jedoch zunächst ein Adsorpt finden, das deutlich zwischen Platin- und Rutheniumatomen unterscheidet. Das heisst, das betreffende Gas darf entweder nur an einer der beiden Atomarten adsorbiert werden, oder aber, wenn eine Adsorption an beiden Elementen auftritt, muss eine messbare physikalische Eigenschaft des

Adsorptionskomplexes für Ruthenium deutlich von der für Platin verschieden sein.
Diese Erwägungen lenkten unser Augenmerk auf Kohlenmonoxyd als mögliches Agens für eine chemisorptive Titration von Pt-Ru-Oberflächen. CO wird, soweit bekannt, von allen Metallen der VIII-ten Nebengruppe stark chemisorbiert und verursacht an den meisten dieser Metalle eine erhebliche Austrittsarbeitserhöhung von rd. 1 eV [7-9]. Platin nimmt in dieser Beziehung jedoch eine Ausnahmestellung ein, da die Austrittsarbeit des Platins durch CO nur um einen sehr geringen Wert (0,05 eV) erhöht wird, wie in einer früheren Veröffentlichung [10] ausführlich berichtet wurde. Da andererseits aus einer kürzlich erschienen Arbeit von Klein [11] hervorgeht, dass CO die Austrittsarbeit von Ruthenium um 1,3 eV erhöht, sollte es möglich sein, durch Messung der durch CO-Adsorption hervorgerufenen Änderung der Austrittsarbeit von Pt-Ru-Filmen Aufschluss über den Ruthenium-Gehalt der Filmoberfläche zu gewinnen. Von den Methoden zur Messung der Austrittsarbeit von Filmen hat die der photoelektrischen Emission den Vorteil, dass sie neben der Austrittsarbeit Φ die Mengenkonstante M als zusätzliche Information liefert. Ausserdem ist sie frei von der Notwendigkeit einer inerten Bezugselektrode und kann bei beliebig niedriger Temperatur angewandt werden.

Nun ist es sehr gefährlich, Austrittsarbeiten und Austrittsarbeitsänderungen bei Chemisorption durch einen einfachen Zahlenwert zu beschreiben, da die Austrittsarbeit bekanntlich stark vom Ordnungsgrad und der kristallographischen Beschaffenheit der Oberfläche abhängt [10,12]. Bevor an eine Anwendung für Pt-Ru-Legierungen gedacht werden kann, ist es daher notwendig, sowohl die photoelektrischen Parameter als auch deren Änderungen durch CO-Adsorption für beide Metalle als Funktion des Temperns genau zu untersuchen. Für das System Pt-CO war über die entsprechenden Ergebnisse in einer vorhergehenden Arbeit [10] berichtet worden, für das System Ru-CO werden die Messdaten nunmehr vorgelegt. Dabei ist es notwendig, den Einfluss des Temperns bis zu so hohen Temperaturen zu untersuchen, wie sie für die Herstellung homogenisierter Legierungsfilme erforderlich sind. Nach unseren früheren Erfahrungen [13], ist für einphasige Legierungen zu erwarten, dass sich bei simultan aufgedampften Filmen das Gleichgewicht innerhalb einiger Stunden bei etwa 0,3 T_f einstellt, wobei T_f der Schmelzpunkt (in °K) der Legierung ist. Diese Erwägung zwang uns dazu, in der vorliegenden Arbeit bis zu Tempertemperaturen T_t von etwa 900°K zu gehen. Da dies mit den Pyrexapparaturen, in denen herkömmlicherweise Metallfilme photoelektrisch untersucht werden, natürlich nicht möglich ist, mussten einige der zu besprechenden Messungen in einer teilweise aus Quarz bestehenden Zelle[14] ausgeführt werden.

Die durch ein Adsorbat hervorgerufene Austrittsarbeitsänderung wird nach den gängigen Theorien proportional dem Produkt aus dem Bedeckungsgrad und dem Dipolmoment der Adsorptionsbindung projiziert auf die Oberflächennormale, angenommen. Wenn die bei gegebenem Druck und gegebener Temperatur durch ein bestimmtes Adsorpt hervorgerufene Änderung der Austrittsarbeit vom Tempergrad des Filmes abhängt, sollte eine der drei Grössen:

a) elementares Dipolmoment

b) Orientierung des Dipols zur Oberflächennormalen,

c) Zahl der adsorbierten Moleküle je cm^2 der Oberfläche,

vom Grad des vorherigen Temperns abhängen. Eine vierte Möglichkeit ist jedoch, dass die bei der Adsorption freiwerdende Wärme bei ungeordneten Filmen ein lokales Tempern verursacht. Um zwischen diesen Möglichkeiten unterscheiden zu können, erschien es uns zweckmässig, an Ru-Filmen verschiedenen Tempergrades auch die physikalische Adsorption von Xenon, bzw. die dadurch hervorgerufene Änderung der Austrittsarbeit zu untersuchen.

2. Experimenteller Teil

Die Versuchsdurchführung war i.allg. die gleiche wie früher[10] beschrieben Ein Teil der Messungen wurde auch mit der dort angegebenen Photozelle (Zelle 1) durchgeführt. Da diese jedoch nur Tempertemperaturen zwischen 78°K und 600°K zuliess, wurde für die bei höheren Temperaturen getemperten Filme eine andere Zelle (Zelle 2) benutzt, in der Filme bis zu 1000°K unter Ultrahochvakuum-Bedingungen getempert werden konnten. Kennzeichnend für diese Zelle ist ein aus Quarz bestehender Kathodenträger, der allseitig von Ultrahochvakuum umgeben ist, so dass die Gasdurchlässigkeit von Quarz bei höheren Temperaturen keinen Einfluss auf die Vakuumbedingungen ausübt. In diesen Träger der über Wolframschienen gleiten und magnetisch von aussen bewegt werden kann, ist ein Tantal-Heizdraht eingebettet. Nachdem dieser Träger einige Wochen lang ununterbrochen bei 1500°K ausgeheizt worden war, war es möglich, auf den Träger aufgedampfte Metallfilme bis zu 1000°K zu erhitzen, ohne dass der Drück über 10^{-10} Torr stieg. Die Temperatur des Kathodenträgers konnte durch ein eingebettetes Thermopaar gemessen werden. Ein Nachteil der Zelle 2 ist, dass der Kathodenträger nicht gekühlt werden kann; die Xenon-Adsorptionsmessungen wurden deshalb in Zelle 1 ausgeführt mit Filmen, die innerhalb der für diese Zelle geltenden Temperaturgrenzen getempert waren.

Die Filme wurden in folgender Weise hergestellt: Spektroskopisch reiner Ruthenium-Schwamm wurde in einem Argonbogen zu Kügelchen geschmolzen. Kügelchen mit einem Durchmesser von 0,1-0,2 mm wurden auf eine Wolfram-Wendel (0,3 mm Ø) geschweisst. Nach Einbau dieser Ru-Quellen in die Photozelle und dem üblichen Ausheizen derselben wurden sie nächst mit Wasserstoff chemisch reduziert. Nach dem Evakuieren auf einem Druck unterhalb 5×10^{-10} Torr wurden sie ausgeheizt. Da hierbei etwa 10% des Rutheniums sublimiert, war während dieses Arbeitsganges der Kathodenträger abgeschirmt, so dass kein Ruthenium auf ihn gelangen konnte.

Während des Aufdampfens auf den Kathodenträger blieb der Druck unterhalb 5×10^{-10} Torr. In Zelle 1 wurde der Kathodenträger während des Aufdampfens auf 78°K gekühlt. Nach 30-minutigem Tempern auf die gewünschte Tempertemperatur T_t und darauffolgendem Abkühlen auf die Adsorptionstemperatur T_a wurde Xenon* (bei $T_a = 78°K$) bzw Kohlenmonoxyd** (bei $T_a = 78°K$, bzw. 293°K) zugelassen und der Photostrom als Funktion der Zeit registriert. Sobald der Film mit dem betreffenden Adsorptiv gesättigt war, was in beiden Fälle unterhalb $p = 10^{-4}$ Torr geschah, wurde die spektrale Empfindlichkeitskurve gemessen. Wenn sowohl Austrittsarbeit als auch Mengenkonstante mit denen des jungfräulichen Films übereinstimmten, was in allen Versuchen der Fall war, wurde anschliessend am gleichen Film

---

* L'Air Liquide, angegebene Reinheit: 99,995%

** L'Air Liquide, angegebene Reinheit: 99,99%

die Chemisorption von CO untersucht.

3. Ergebnisse

Der Einfluss der Tempertemperatur auf die Austrittsarbeit des reinen Rutheniums ist in einer anderen Veröffentlichung[15] beschrieben, die Ergebnisse sind in Abb. 1 zusammengefasst. Das Ruthenium bestätigt die mit anderen Elementen gemachte Erfahrung, dass die Austrittsarbeit mit der Tempertemperatur zunimmt und bei etwa $T_t = 0{,}3\ T_f$ einen konstanten Endwert erreicht.

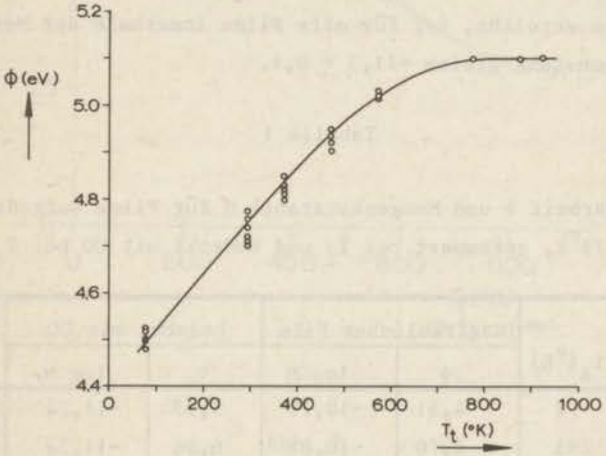


Abb. 1

Austrittsarbeit von Ruthenium-Filmen in Abhängigkeit von der Tempertemperatur.

Die Änderung sowohl der Austrittsarbeit als auch der Mengenkonstanten bei Chemisorption von CO an Filmen, die vorher bei verschiedenen Temperaturen getempert worden waren, sind in Tabelle 1 zusamengestellt. Die Änderung der Austrittsarbeit $\Delta\Phi$ ist in Abb. 2 als Funktion der vorhergehenden Tempertemperatur T_t aufgetragen. Hierbei erscheinen die folgenden Punkte bemerkenswert:

1. $\Delta\Phi$ nimmt ab von 1,44 eV für ungetemperte Filme auf 0,58 eV für

bei 873°K getemperte Filme. Dieser Trend bleibt auch dann eindeutig, wenn man den Messpunkt bei 78°K, wegen der Möglichkeit schwach gebundener Komplexe zusätzlich zum stabilen Chemisorptionskomplex, ausser Betracht lässt.

2. Der Endwert, den die Austrittsarbeit nach Tempern und CO-Adsorption erreicht, ist für Tempertemperaturen bis zu etwa 500°K konstant gleich 6,0 ± 0,1 eV. Bei höheren Tempertemperaturen ist der Endwert niedriger.
3. Der Endwert, den die Mengenkonstante (log M) nach Tempern und CO-Adsorption erreicht, ist für alle Filme innerhalb der Messfehlergrenzen konstant gleich -11,3 ± 0,1.

Tabelle 1

Austrittsarbeit Φ und Mengenkonstante M für Filme aufgedampft bei 78°K, getempert bei T_t und bedeckt mit CO bei T_a

T_t(°K)	T_a(°K)	jungfräulicher Film		bedeckt mit CO		$\Delta\Phi$
		Φ	log M	Φ	log M	
78	78	4,51	-10,79	5,95	-11,34	1,44
293	293	4,70	-10,51	6,06	-11,24	1,35
380	293	4,79	-10,49	6,00	-11,32	1,21
473	293	4,82	-10,57	6,05	-11,39	1,13
573	293	4,97	-10,82	5,81	-11,37	0,84
873	293	5,11	-11,27	5,69	-11,28	0,58

Die Ergebnisse einiger Desorptionsversuche sind in Tabelle 2 zusammengestellt. Sie wurden in Zelle 1 ausgeführt, da in Zelle 2 das desorbierte CO mit dem glühenden Wolframdraht in Berührung kommen würde, wobei CO_2-Bildung durch die Boudouart-Reaktion möglich wäre.

Die Ergebnisse der Adsorption von Xenon sind aus Tabelle 3 und Abb. 3 zu entnehmen. Es zeigt sich, dass im schroffen Gegensatz zur CO-Adsorption, die durch Xenon verursachte Austrittspotentialsänderung unabhängig von der Sintertemperatur des Films ist. Die Austrittsarbeit wird

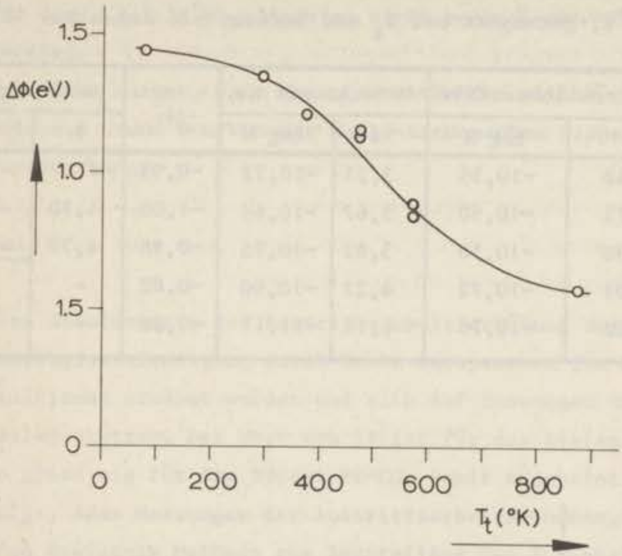


Abb. 2

Zunahme von Φ_{Ru} durch Bedeckung mit Kohlenmonoxyd, in Abhängigkeit von der Sintertemperatur.

Tabelle 2

Desorptionsversuch

Zustand	Φ	log M
Bedeckt mit CO	5,96	-11,31
T_{des} = 488°K	5,82	-11,21
T_{des} = 573°K	5,42	-10,70
Jungfräulicher Film	4,97	-10,83

Tabelle 3

Austrittsarbeit Φ und Mengenkonstante M für Filme aufgedampft bei 78°K, getempert bei T_t und bedeckt mit Xenon bei 78°K

T_t (°K)	jungfräulicher Film		bedeckt mit Xe		ΔΦ	nach Abpumpen	
	Φ	log M	Φ	log M		Φ	log M
78	4,48	-10,56	3,53	-10,72	-0,95	-	-
293	4,72	-10,50	3,67	-10,69	-1,05	4,70	-10,50
373	4,80	-10,50	3,82	-10,75	-0,98	4,79	-10,50
473	5,03	-10,72	4,21	-10,90	-0,82	-	-
573	5,02	-10,76	4,14	-11,11	-0,88	-	-

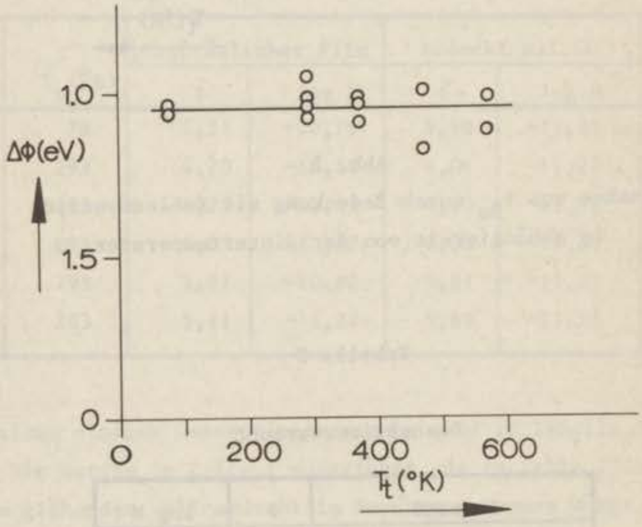


Abb. 3

Abnahme von Φ_{Ru} durch Bedeckung mit Xenon, in Abhängigkeit von der Tempertemperatur.

um 0,95 ± 0,05 eV herabgesetzt. Wie bereits erwähnt, ist der Effekt vollkommen reversibel. Die Mengenkonstante wird durch Xenon herabgesetzt. Auffällig ist, dass Xenon auch bei 143°K (Pentanschmelze) noch reversibel adsorbiert wird. Bei 78°K gelingt es nicht mehr, Xenon durch Abpumpen zu desorbieren.

Diese Ergebnisse zeigen, dass Xenon an Ruthenium erheblich fester gebunden ist als auf Grund von Van der Waals-Londonschen Dispersionskräften erklärt werden kann.

4. Diskussion

Die grossen Absolutwerte der Austrittsarbeitserhöhung durch CO, sowie der Austrittsarbeitserniedrigung durch Xenon entsprechen den Erwartungen, die in der Einleitung erwähnt wurden und sich auf Messungen an anderen Übergangsmetallen stützen. Der Wert von $\Delta\Phi$ ist für das System Ru-CO rund 20 mal so gross wie für das System Pt-CO. Damit erscheint der Schluss gerechtfertigt, dass Messungen der Austrittsarbeitserhöhung bei Adsorption von CO eine geeignete Methode zur Beurteilung des Ru-Gehaltes der Oberfläche von Pt-Ru-Legierungen bieten. Die wichtigste Frage, die diese vorliegende Untersuchung motivierte, ist somit positiv beantwortet.

Die für CO gefundene Erhöhung der Austrittsarbeit stimmt auch mit dem inzwischen bekannt gewordenen Ergebnis von Klein[11] überein, der eine Austrittsarbeitszunahme von 1,3 eV fand. Allerdings sind andere Mitteilungen in der gleichen Arbeit nicht mit unseren Ergebnissen in Übereinstimmung. Klein findet eine sehr geringe Adsorptionswärme von CO auf Ru, der zufolge schon bei 225°K eine merkbare und oberhalb 500°K eine praktisch vollständige Desorption von CO eintreten soll. In unseren Versuchen, sind die Messdaten bei 78°K und 293°K für vorgesinterte Filme praktisch gleich, während nach Desorption bei 573°K die Austrittsarbeit noch um 0,45 eV über dem Wert des bei der gleichen Temperatur gesinterten jungfräulichen Film liegt. Wir schliessen hieraus, dass auch nach Desorption bei 573°K noch erhebliche CO-Mengen auf der Oberfläche chemisorbiert bleiben. Selbst wenn man postuliert, dass die vorübergehende Anwesenheit von CO ein Sintern der Oberfläche und damit eine auch nach dem Desorbieren nicht reversibele Änderung der Austrittsarbeit hervorruft, ist man gezwungen, aus dem Endwert von Austrittsarbeit und Mengenkonstanten auf die Anwesenheit von noch adsorbiertem CO zu schliessen, da beide Grössen sich noch erheblich von den Endwerten unterscheiden, die nach langem Sintern reiner Filme bei viel höherer Temperatur beobachtet wurden.

Während die Zunahme der Austrittsarbeit von reinem Ruthenium mit zunehmender Tempertemperatur bis zum Wert $T_t = 0{,}3\ T_f$ einer allgemeinen Erfahrung entspricht und an anderer Stelle ausführlich erörtert wird, ist die starke Abhängigkeit der durch CO-Adsorption verursachten Änderung $\Delta\Phi$ von der Temperatur des vorherigen Sinterns ein neuer Befund, der eine eigene Diskussion an dieser Stelle rechtfertigt.

In der Einleitung wurde bereits erwähnt, welche physikalischen Grössen für den Wert von $\Delta\Phi$ verantwortlich sind.

Zu diskutieren ist also, wieso ein Sintervorgang, der im wesentlichen Gitterfehler beseitigt, dazu führt, dass die nachfolgende Adsorption von CO zu einem kleineren $\Delta\Phi$-Wert führt.

In der Vergangenheit[16] war darauf hingewiesen worden, dass das Moment des Bindungsdipols von der Differenz $(\Psi - \Phi)$ bestimmt werden kann, wobei Ψ die Elektronegativität des Adsorptivs und Φ die Austrittsarbeit des Adsorbens ist. Diese Hypothese würde unsern Befund erklären, dass für CO mit gegebenem Ψ die Grösse von $\Delta\Phi$ mit zunehmendem Φ abnimmt. Trotzdem glauben wir, dass diese Erklärung im vorliegenden Falle nicht anwendbar ist, da nach dieser Hypothese die Abnahme der Austrittsarbeit durch adsorbiertes Xenon für die gesinterten Filme grösser sein müsste als für ungesinterte, was den gemessenen Ergebnissen widerspricht.

Auch die Annahme von zwei nebeneinander auftretenden Ru-CO-Komplexen verschiedener Polarität erscheint ungenügend, die Befunde zu erklären. Das für andere Übergangsmetalle vorliegende Tatsachenmaterial zeigt, dass der Chemi-Adsorptionskomplex für CO die Austrittsarbeit erhöht, wogegen die korrosive Chemisorption zu einer relativen Erniedrigung von Φ führt[17]. Da korrosive Chemisorption aber gerade an den atomar rauhen Kristallflächen überwiegt, die während des Sinterns weitgehend verschwinden, würde diese Überlegung für durch Sintern geglättete Flächen eher einen erhöhten $\Delta\Phi$-Wert erwarten lassen.

Die Annahme zweier Komplexe mit negativem Ad-Dipolmoment auf verschiedenen Kristallflächen kann den Befund der Abb. 2 nur dann erklären, wenn man annimmt, dass auf den rauhen Kristallflächen im Vergleich zu den glatten

Flächen a) entweder der Ad-Dipol stärker negativ ist,
b) oder der Bedeckungsgrad erheblich höher ist als auf den glatten Flächen.

Diese Möglichkeiten können durch die vorliegenden Ergebnisse zwar nicht ausgeschlossen werden, sind aber insofern unbefriedigend, als sie den gemeinsamen Endwert nach CO-Adsorption sowohl der Austrittsarbeit als auch der Mengenkonstanten von bei verschiedenen Temperaturen gesinterten Filmen unerklärt lassen.

Wir glauben, dass nach dem Verwerfen der genannten Hypothesen unsere Ergebnisse, sowie die Literaturdaten über korrosive Chemisorption den Schluss nahe legen, dass bei der Chemisorption von CO an ungesinterten Filmen die freiwerdende Adsorptionswärme zu lokalen Umgruppierungen von Ru-Atomen führen kann[17,18], wobei noch vorhandene Gitterfehler weitgehend verschwinden. Infolgedessen befinden sich vorher ungesinterte Filme nach Bedeckung mit CO in demselben Zustand wie Filme, die bereits vor der Adsorption gesintert worden waren. Hiermit stimmt die Tatsache überein, dass sowohl die Austrittsarbeit als auch die Mengenkonstante nach Adsorption von CO für die bei 78°, 293°, 380° und 473°K vorgesinterten Filme die gleichen Werte haben. Die Hypothese des durch CO Chemisorption induzierten Temperns ungeordneter Filme wird weiterhin bestätigt durch die Ergebnisse der Adsorption von Xenon. Da die bei der physikalischen Adsorption freiwerdende Energie zu klein ist, um ein lokales Sintern zu induzieren, ist hier $\Delta\Phi$ unabhängig vom Ordnungsgrad der adsorbierenden Filme.

Die geringfügige Abnahme von Φ_{CO} für sehr hoch gesinterte Filme (T_t = 573°K, bzw. 873°K, siehe Tabelle 1) deutet daraufhin, dass bei diesen Filmen mit besonders glatter Oberfläche die gegenseitige Depolarisation der Oberflächendipole[19] stärker ist als bei rauhen Oberflächen, wo diese Dipole besser gegeneinander abgeschirmt sind.

Die Untersuchungen wurden unterstützt von der Niederländischen Stiftung für Chemische Forschung (S.O.N.) mit einer Subvention der Niederländischen Organisation für reinwissenschaftliche Forschung (Z.W.O.).

Wir danken den Herren Drs. H.P. van Keulen und G.J.M. Lippits für ihren Beitrag zu den Messungen und F.C. Kauffeld für die sinnreiche Entwicklung und den Bau der Photozelle.

Literatur

1) D.W. McKee und F.J. Norton, J. Phys. Chem 68, 481 (1964).

2) G.C. Bond und D.E. Webster, Platinum met. rev. 10, 10 (1966).

3) W.M.H. Sachtler und G.J.H. Dorgelo, J. Catalysis 4, 654 (1965).

4) P. van der Plank und W.M.H. Sachtler, J. Catalysis 7, 300 (1967).

5) P. van der Plank und W.M.H. Sachtler, J. Catalysis 12, 35 (1968).

6) R. Bouwman und W.M.H. Sachtler, J. Catalysis, im Druck.

7) F. Bloyaert, L. D'Or und J.C.P. Mignolet, J. Chim. phys. 54, 53 (1957)

8) R.V. Culver, J. Pritchard und F.C. Tompkins, Proc. 2nd Int. Congr. Surface Act. Vol. 2, p. 243, Butterworths, London (1957).

9) R. Suhrmann, H. Ober und G. Wedler, Z. phys. Chem. N.F. 29, 305 (1961)

10) R. Bouwman, H.P. van Keulen und W.M.H. Sachtler, Ber. Bunsenges. physik. Chem. 74, 198 (1970).

11) R. Klein, Surface Science 20, 1 (1970).

12) R. Suhrmann und G. Wedler, Z. angew. Physik, 14, 70 (1962).

13) R. Bouwman und W.M.H. Sachtler, Surface Sci. im Druck.

14) R. Bouwman und F.C. Kauffeld, unveröffentlicht.

15) R. Bouwman und W.M.H. Sachtler, Surface Sci. im Druck.

16) W.M.H. Sachtler, Z. Elektrochemie 59, 119 (1955).

17) A.A. Holscher und W.M.H. Sachtler, Disc. Faraday Soc. 41, 29 (1966).

18) M.W. Roberts, "Recent Progress in Surface Science", Vol. 3, Acad. Press N. York (1970) p. 1 - 22.

19) J.H. de Boer: "Electron Emission and Adsorption phenomena", Cambridge, At the University Press (1935).

Chapter VI

PHOTOELECTRIC DETERMINATION OF THE WORK FUNCTION OF GOLD-PLATINUM ALLOYS *

by
R. Bouwman and W.M.H. Sachtler

Afdeling Heterogene Katalyse
Chemische Laboratoria, Rijksuniversiteit, Leiden
the Netherlands

Summary

Films of platinum, gold and their alloys were prepared by vapour deposition of the metals - either simultaneously or successively - and subsequent sintering under ultra-high vacuum.

The photoelectric emission of these films was investigated and it was found that equilibrated alloys of compositions within the miscibility gap of the Pt-Au phase diagram possessed identical work functions. This agrees with the expectation, based on thermodynamic and diffusion data, that the gold-rich alloy should envelop crystallites of the co-existing Pt-rich alloy.

The work function of the gold-rich alloy is lower than that of gold or that of platinum.

These results are completely analogous to those found previously for the Cu-Ni system.

The previously predicted dependence of surface composition on the surrounding gas atmosphere has been experimentally verified.

---

* Journal of Catalysis, in press.

Carbon monoxide causes an enrichment of the platinum in the surface. This process takes several days at room temperature and may be reversed by pumping off the carbon monoxide at elevated temperature.

1. Introduction

In previous work[1-5] it was shown that the surface composition of clean copper-nickel alloy films, prepared by evaporation of the metals under ultra-high vacuum followed by sintering at 200°C, is constant and independent of the bulk composition within the limits of the miscibility gap of this system.

For these films the photoelectric work function[1], the catalytic activity for certain test reactions[4,5] and the chemisorption of hydrogen per unit of surface area[4] were found to be constant.

These results were interpreted in terms of a model based on thermodynamic[6,7] and diffusion data[8,9]. The model assumes that after sintering the films are built up of crystallites, each of which consists of a kernel of a nickel-rich alloy envelopped by a mantle of a copper-rich alloy.

The formation of this peculiar arrangement is a consequence of two essential properties of the copper-nickel system:

1. It possesses a miscibility gap.
2. The diffusion rate of one metal (i.e. copper) is significantly greater than that of the other.

The predictions of this model were recently confirmed for granular copper-nickel alloys by Cadenhead and Wagner[10]. As the model makes use of simple physical laws, one should also be able to predict the surface composition and hence also the chemisorption behaviour of related alloy systems.
In this respect the platinum-gold system appears almost ideal for checking the basic principles used. The platinum-gold system is known to possess a wide miscibility gap[11,12] for temperatures below 1258°C as follows from the phase diagram shown in Fig. 1. The system also satisfies the second condition, the diffusion of gold being considerably faster than that of

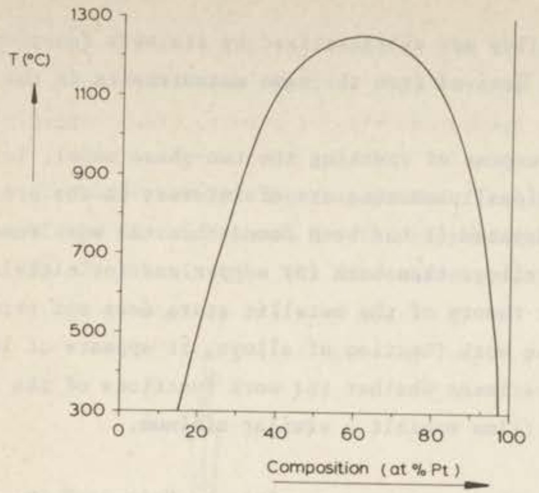


Figure 1

The phase diagram for gold-platinum alloys.

platinum. The Kirkendall effect in Au-Pt alloys was proved and studied by Bolk[13,14].

Although equilibration might be extremely slow for bulk alloys, the results obtained with the copper-nickel system showed that for thin films, prepared under ultra-high vacuum, equilibration is possible at moderate temperatures.

It may, therefore, be expected that for platinum-gold films a surface of constant Pt-Au ratio in the film will be obtained for all alloys with compositions within the miscibility gap. Moreover, we expect that the Pt-Au ratio in the surface should be that of the stable gold-rich alloy at the left-hand edge of the miscibility gap.

In the present article work is described to check these principles. For this purpose platinum-gold alloy films were prepared under ultra-high vacuum by various techniques including successive and simultaneous vacuum deposition of the two metals followed by sintering. The films obtained were then studied by using them as cathodes in photoelectron emission.

In this way each alloy was characterized by its work function ϕ.

A second parameter derived from the same measurements is the emission constant M.

Besides the main purpose of checking the two-phase model, for equilibrated films, three additional phenomena are of interest in the present work:

a) For the Cu-Ni system it has been found that the work function is lower for the alloys than both for copper and for nickel.

   As the present theory of the metallic state does not permit any prediction for the work function of alloys, it appears of interest to explore by experiment whether the work functions of the equilibrated platinum-gold films exhibit a similar minimum.

b) In the Cu-Ni work it appeared possible to "titrate" the surface composition by chemisorption of a gas which is selective for nickel. We, therefore, thought it worthwhile to study the change in work function of platinum-gold films caused by chemisorption of carbon monoxide.

   This gas is known to be chemisorbed rather strongly by platinum, its heat of adsorption being at least 30 Kcal/mol[15,16], but not by gold, at room temperature.

c) The composition of any alloy surface in thermodynamic equilibrium should, in principle, be dependent upon the surrounding atmosphere. The energy of a Pt/Au-CO system would be lowered by enriching the surface with Pt-atoms which can form strong chemisorption bonds with CO molecules. A dependence of the surface composition on the contacting atmosphere has repeatedly been postulated for alloys[2,17], but has never been confirmed experimentally.

   The Cu/Ni-CO system proved to be unsuitable for this purpose because of the formation of gaseous nickel tetracarbonyl on the nickel parts of the cell and the decomposition of this compound on the alloy surfaces causes such a drastic change in the surface composition that a possible simultaneous slow diffusion of metal atoms to the surface cannot be observed. In this respect the Pt/Au-CO system provides much better prospects.

2. Experimental

a) The phototubes

Two types of phototubes have been used. The first one, based on the principle of the phototube used for the copper-nickel system[1] is shown in Fig. 2. In this tube (I) successive evaporation of the metals is carried out whereas in the other phototube (II) shown in Fig. 4 simultaneous evaporation of both metals is also possible.

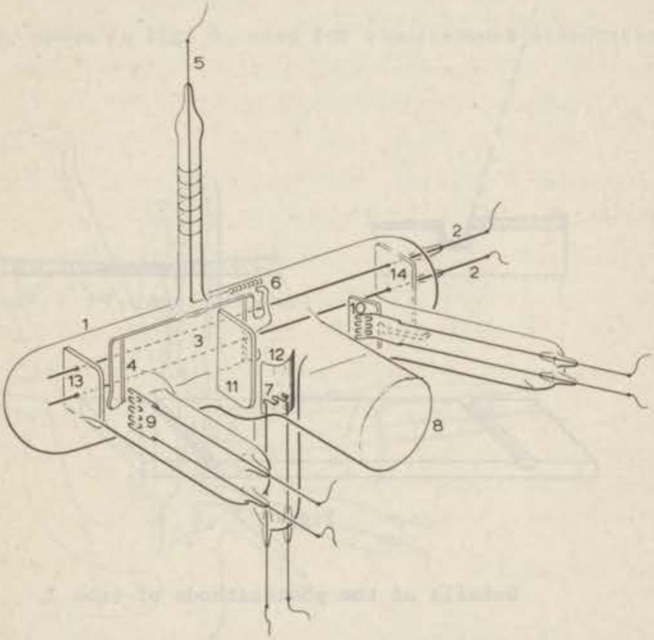


Figure 2

Phototube, type I.

The first phototube consists of a pyrex housing (1) having a diameter of 50 mm. Through one end, two elongated parallel tungsten rods (2) are fused. A polished pyrex cathode (3) sliding over these rods on four small tubes is provided with a glass-clad iron bar in order to make magnetic operation possible from the exterior. The surface of the cathode, to be coated with the alloy films, is in electrical contact with the tungsten rods through fused platinum rods and spirally wound polished platinum wire embedded in the inner surface of the slide tubes. The cathode surface is provided with two slots (4) having a width of 1 mm and a depth of 1 - 2 mm , in order to separate film segments from each other (see Fig. 3). These slots prevent lateral diffusion of metal atoms across metal or alloy surfaces between film segments. The anode of the phototube consists of a tungsten rod (5) carrying a small platinum wire (6) embedded at a suitable position in the interior of the phototube. The tungsten rod is surrounded by a double quartz-to-pyrex transition in order to ensure the extreme insulation required for reliable measurements of photocurrents in the range of $10^{-13} - 10^{-15}$ Amp.

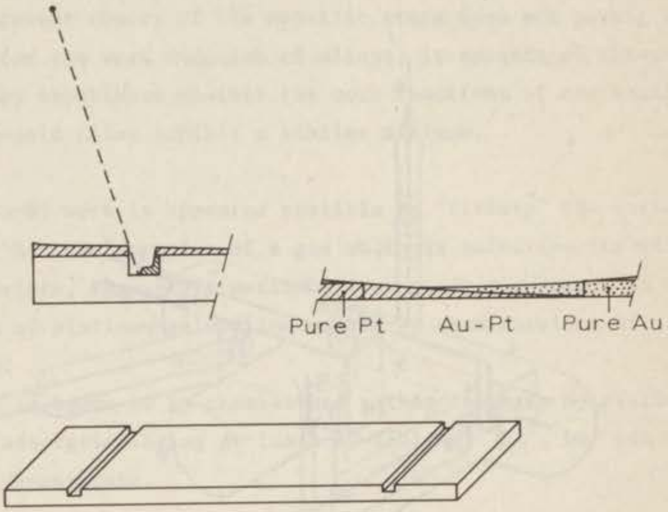


Figure 3

Details of the photocathode of tube I.

Gold evaporated from the source (7) forms the anode screen in contact with the platinum wire (6) in the upper section of the phototube. A planparallel quartz window (8) is arranged parallel to the photocathode.

The two metal sources (9, 10) are situated on either side of the quartz window with a glass screen (11) to shield part of the cathode during evaporation of one metal. In this way the pure metals are obtained on the terminal zones and a concentration gradient is obtained in the alloys in intermediate positions. A screen (12) protects the quartz window from evaporated gold from source (7). Two screens (13, 14) are placed at the terminals of the tungsten rods (2). Screen (13) serves as a support for the rods, while screen (14) protects the anode and cathode outputs from internal shorting due to the presence of a condensed metal film.

Phototube (II), shown in Fig. 4, used for simultaneous evaporation, consists of a Dewar type tube (1) terminating in a polished cathode (2) provided with similar current-transporting platinum rods (3) fused within the glass and connected to a cathode lead (4). Magnetically movable shutters (5, 6) protect the terminal zones of the cathode which are reserved for the deposition of the pure metals. The anode (7) resembles that of tube (I). The anode metal film in contact with the em-

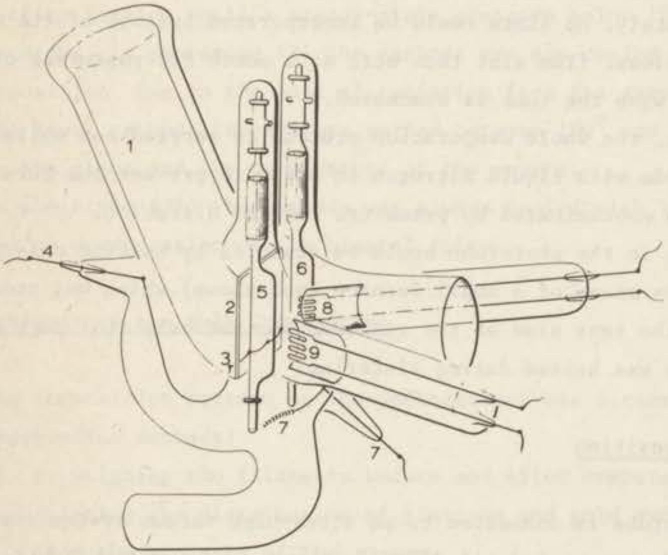


Figure 4

Phototube, type II.

bedded platinum wire (7) is formed during evaporation of the two metals to be studied. In tube (II) the sequence: gold - alloys - platinum was formed as follows:

1) A small proportion, roughly 10%, of the first metal, (e.g. (8)) is evaporated with shutter (6) in the open position and shutter (5) closed, i.e. pressed flatly onto the cathode.
2) Subsequently, a similar proportion of the other metal (9) is evaporated with the shutter (5) in the open position and shutter (6) closed.
3) Finally, both shutters are closed and the remainder of both metals is evaporated simultaneously.

Unfortunately, no slots could be incorporated because of the danger of implosions. (The slot then acts as a notch for rupturing of the cathode, when the tube is evacuated.)
Therefore, the whole evaporation process is carried out while cooling the cathode with liquid nitrogen in order to prevent the pure metals to become contaminated by premature lateral diffusion.
The films in the phototube could be sintered by heating only the cathode by means of a small furnace (not shown) which was pressed against the rear side of the cathode, so that only that part of the phototube was heated during sintering.

b) Metal Deposition

The phototube is connected to an ultra-high vacuum system evacuated by Edwards rotary and oil diffusion pumps and a Varian Vac-Ion pump. Ultra-high vacuum is attained by several bakeouts each lasting about 15 hours, at a temperature between 400° and 450°C.
Metals are evaporated only when the residual gas pressure is below 3.10^{-10} Torr. Before depositing a film on the photocathode a small proportion of each metal is evaporated while the cathode is shielded completely behind screen (11) (Fig. 1). By means of this preevaporation volatile impurities are removed so that during subsequent evaporation the pressure will remain below 5.10^{-10} Torr.
With gold, it proved difficult to maintain a pressure in the range of 10^{-10} Torr, during evaporation. This metal was, therefore, pretreated

before bakeout by heating it above its melting point in hydrogen at a pressure of 5-10 Torr. This treatment greatly improved the vacuum during the subsequent deposition of gold.

Both metals were evaporated from specially shaped tungsten filaments, spotwelded to tungsten rods. Due to the shape of the filaments, resembling a recurring hair-pin, relatively large amounts of platinum could be evaporated without blowing of the filament. Moreover, this special shape had the advantage that very uniform evaporation was achieved in a predictable way. The filaments were always reduced in a hydrogen atmosphere. After the first bakeout-run, the supporting tungsten rods of the filaments were degassed by high-frequency induction heating until a steady-state pressure below 10^{-8} Torr was recorded. In phototube (I) the cathode was not cooled during film deposition. Due to the heat of radiation from the evaporation sources the local cathode temperature varied between 100° and 200°C depending on the place and the temperature of the source.

In phototube (II) the cathode was always cooled with liquid nitrogen during condensation of the bimetal films.

c) Analysis of the Bulk Composition

The composition pattern on the photocathode was determined by two independent methods:

1) By weighing the filaments before and after evaporation and calculating the distribution of platinum and gold over the cathode from the geometry of the system.
2) By neutron activation analysis.
   For this purpose, the alloy film strips of interest were dissolved in a small amount of aqua regia prepared from p.a. acids. The solutions were absorbed in ultra clean filtration paper obtained by elution with 0.1N HCl during 20 hours followed by elution with conductowater during 40 hours and drying. The analyses were carried out at the Reactor Institute of the Technical University of Delft*.

---

* The authors are indebted to Professor P.J. Houtman and his coworkers for the analysis of the photocathode.

The results of both analytical methods agreed within 5% and were averaged. The removal of the strips of the film from the pyrex substrate gave rise to the largest errors. We estimated the accuracy of the reported bulk values at about ± 3at%.

The bulk alloy composition of the cathode was also investigated by X-ray diffraction* in reflection.

d) Determination of the Work Function and the Emission Constant

Light from an air-cooled, high-pressure mercury lamp passing through a Bausch & Lomb grating monochromator was focussed via a mirror system onto either the desired location on the photocathode or on a calibrated tantalum reference tube.

The photocurrent obtained, is amplified by an E.I.L. vibrating reed electrometer, type 51A. The phototubes were coated with a grounded "Aquadag" layer to protect them against external electromagnetic stray fields. Residual fields penetrating to the cathode limited the lower value of reliable measurements of photocurrents to 10^{-14} Amp.

According to the theory of Fowler, the photoelectric yield I in electrons emitted per photon is related to the frequency ν of the light by

$$I = M.T^2\{ \frac{\Pi^2}{6} + \frac{x^2}{2} - (e^{-x} - \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} - \cdots\cdots)\} \qquad (1)$$

where M is the emission constant expressed in electrons.photon^{-1}. degree^{-2}, T is the absolute temperature and $x = \frac{h\nu - h\nu_o}{kT} = \frac{E - \Phi}{kT}$, where ϕ is the work function and $E = h\nu$, the energy per photon, both expressed in electron volts. For $x >> 1$ or $\nu >> \nu_o$, (1) becomes in good approximation:

$$I = \frac{M (E - \Phi)^2}{2k^2} \qquad (2)$$

By plotting $\sqrt{I}$ against the energy E of the light one obtains ϕ from the intercept on the abcissa and $\sqrt{\frac{M}{2k^2}}$ as the slope of the straight line. In most instances, the work functions could be evaluated with

---

* The authors are very grateful to the contribution of Dr. G.C. Verschoor with regard to these measurements.

an accuracy within ± 0.005 eV and the emission constants could be determined with an accuracy of about 1.10^{-12} electrons.photon^{-1}.degree^{-2}.
The photoelectric yield I is obtained from the recordings of the photocurrents at each frequency by the equation.

$$I = \frac{i_x}{i_{Ta}} . I_{Ta} \qquad (3)$$

where i_x is the photocurrent of the unknown metal or alloy, i_{Ta} is the photocurrent of the calibrated tantalum reference tube and I_{Ta} is the photoelectric yield of this reference tube in electrons per photon.
Our tantalum tube had been calibrated in the Institut für Physikalische Chemie of the Technische Hochschule, Hannover (W.-Germany) against the standard cells used by Professor Suhrmann, Professor Wedler and their collaborators to whom we are indebted for providing this opportunity of creating a common standard reference.

3. Results

The results will be described in terms of four typical experiments, viz.:

I) Gold on top of platinum.
II) Platinum on top of gold.
III) Films prepared by simultaneous deposition of both metals.
IV) Chemisorption of carbon monoxide on alloy films.

a) Experiment I: The freshly deposited bimetal films were investigated immediately after evaporation and again after sintering at 200°C during 16 hours. The results are summarized in Table I and plotted in Fig. 5.
For the fresh films, prior to sintering, a gold-like character is detected throughout almost the entire range of alloy compositions. The work function deviates from the gold value only in the region very rich in platinum.
After sintering at 200°C, the work function of gold has increased to 5.40 eV while most of the other values have increased slightly.
It may be significant that the work functions of some intermediate compositions is now below those of the pure sintered metals. The increase in work function due to sintering of the pure metals is a common phenomenon for most metals, usually explained by assuming that unstable crystal planes and lattice faults disappear from the surface. The increase in work function of some platinum-gold segments can be explained by the same phenomenon of crystallographic ordering and/or to some degree by diffusion

TABLE I

Experiment I: Gold on top of platinum

at% Pt	Φ_{fresh} (eV)	$M_{fresh} \times 10^{12}$ $\left(\frac{\text{electrons}}{\text{photon . deg}^2}\right)$	$\Phi_{sintered}$	$M_{sintered}$
0	5.36	10.1	5.40	6.8
11	5.36	10.3	5.37	6.5
17	5.36	10.1	5.37	6.7
26	5.36	9.9	5.37	6.7
36	5.36	10.2	5.39	6.7
47	5.36	10.4	5.40	7.5
60	5.36	11.4	5.40	8.1
72	5.38	13.7	5.40	10.6
80	5.40	14.0	5.39	10.0
87	5.43	13.7	5.43	8.7
92	5.45	13.7	5.44	9.5
95	5.45	13.7	5.44	9.5
100	5.70	25.1	5.72	28.2

of platinum atoms from deeper layers to the surface of the film. Although it is very difficult to derive reliable and easily understandable information from emission constants which depend on many factors (penetration depths of the photons, escape depth of the electrons, absorption and reflection coefficients, surface area of the film, number and character of dislocation, etc.) the conclusion may be drawn that incomplete equilibration of the films has occurred.

In order to study the effects of lateral diffusion, the work function of Pt was measured in the immediate vicinity of the slot both before and after sintering. While the value, before sintering, was the same on both edges, that of the film in contiguous contact with the composite film showed a lower value after sintering. This is a fair indication for lateral diffusion of gold across the platinum surface.

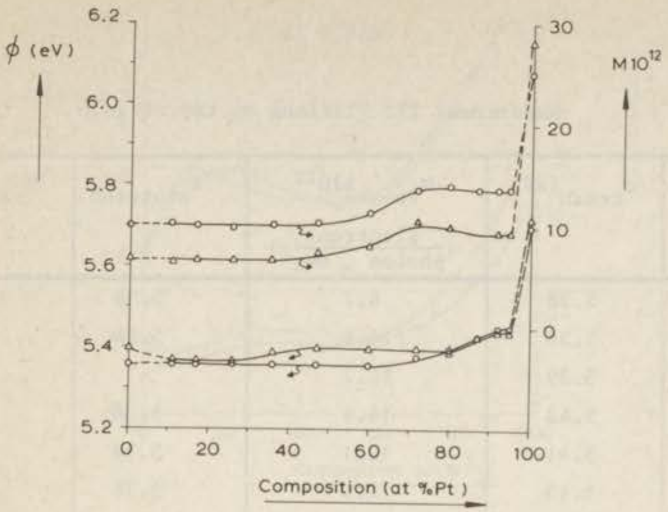


Figure 5

The work functions (lower curves) and emission constants (upper curves) of a film prepared by evaporating gold on top of platinum (experiment I).

○ fresh films

Δ film sintered at 200°C

This phenomenon was not detected at the pure gold edge of the cathode. These data suggest, that gold diffuses rather easily across the platinum surface, whereas platinum diffusion is not detected. This difference in surface diffusion rates is not surprising. Data reported by Bolk[13,14] also show enhanced diffusion rates for gold in bulk samples.

b) Experiment II: Platinum on top of gold

The results of this experiment are compiled in Table II and plotted in Fig. 6.

Again a rather gold-like character is detected at the gold-rich side of the alloy system, but the work function rises sharply from about 60at% of platinum to pure platinum, with an intermediate maximum at about 95at% of platinum.

TABLE II

Experiment II: Platinum on top of gold

at% Pt	Φ_{fresh}(eV)	$M_{fresh} \times 10^{12}$ $\left(\frac{\text{electrons}}{\text{photon} \cdot \text{deg}^2}\right)$	$\Phi_{sintered}$	$M_{sintered}$
0	5.38	6.7	5.38	6.5
12	5.36	14.0	5.34	15.0
19	5.39	14.2	-	-
28	5.42	14.4	5.38	12.5
39	5.41	12.1	5.38	11.7
52	5.40	12.0	5.38	11.7
65	5.42	13.3	5.40	14.4
74	5.49	18.1	5.45	18.8
84	5.60	23.8	5.53	24.6
90	5.70	28.7	5.58	27.1
93	5.75	29.2	5.64	30.0
100	5.70	27.4	5.73	23.6

A shallow minimum at about 12 at% Pt appears prior to sintering. Sintering at 200°C causes effects markedly different from those observed in experiment I. The work functions of all alloy compositions now decrease. The work function of gold remains unchanged and that of platinum increases. The constancy of the work function of gold upon sintering in experiment II can be understood as in this case the gold film was exposed to the high heat of radiation during the subsequent deposition of the platinum film. Therefore, the gold film in the "fresh" state is in fact already presintered. Also the fact that the measured value of the non-sintered film at 12 at% Pt lies below those of pure gold and platinum suggests that some equilibration of the film has been effected, most probably due to the higher heat of radiation during deposition of the second metal, as compared with experiment I. The observed decrease in work function of the alloys upon sintering in experiment II is in agreement with our expectation.

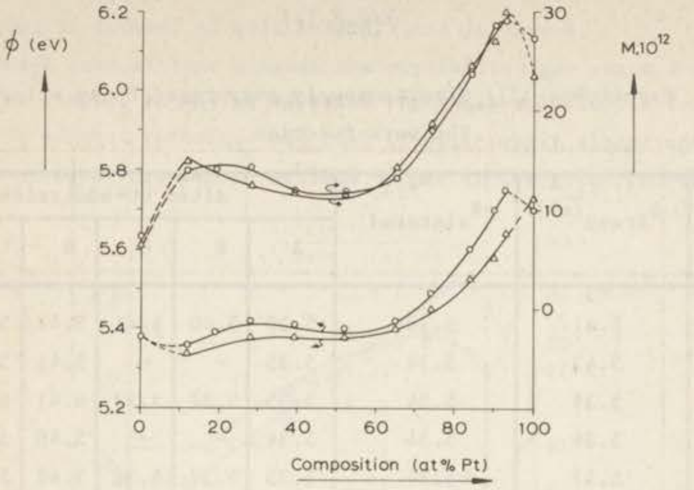


Figure 6

The work functions (lower curves) and the emission constants (upper curves) of a film prepared by evaporating platinum on top of gold (experiment II).

o fresh films

Δ film sintered at 200°C

From the different rates of diffusion it is clear that diffusion from deeper layers of gold (exp. II) should be faster than that of platinum (exp. I). The emission constant shows hardly any dependence upon the alloy composition. Sintering at 200°C did not change the emission constant of gold substantially because platinum was evaporated last in contrast to experiment I. The emission constant of platinum after sintering is even lower than before, again in contrast to experiment I.

c) <u>Experiment III</u>: Simultaneously deposited metals

After our preliminary experiments in phototube (I), experiments III were carried out in phototube (II). In this tube the alloy films were prepared by simultaneous deposition on a cathode cooled by liquid nitrogen. Immediately after deposition of the alloy film, the cathode was heated at room temperature and the spectral distribution curve was measured, the

TABLE III

Experiment III: Simultaneously evaporated Pt-Au alloys

The work function

at% Pt	Φ_{fresh}(eV)	$\Phi_{sintered}$	after CO-admission					F
			A	B	C	D	E	
0	5.41	5.38	5.39	5.40	5.41	5.42	5.43	5.37
15	5.42	5.34	5.35	-	-	5.41	5.43	5.35
20	5.35	5.34	5.35	5.37	5.37	5.41	5.43	5.35
25	5.36	5.34	5.34	-	-	5.40	5.44	5.35
31	5.37	5.34	5.35	5.37	5.38	5.42	5.45	5.34
40	5.38	5.34	5.35	-	5.39	5.42	5.45	5.35
51	5.41	5.34	5.35	5.38	5.39	5.43	5.45	5.35
59	5.44	5.34	5.36	5.38	-	5.45	5.48	5.34
66	5.48	5.35	5.37	5.39	5.42	5.47	5.49	5.34
73	5.52	5.35	5.38	-	-	5.49	5.50	5.34
79	5.56	5.36	5.39	5.42	5.45	5.50	5.51	5.35
84	5.59	5.37	5.41	-	5.46	5.52	5.52	5.36
88	5.58	5.38	5.43	5.45	5.48	5.51	5.53	5.34
100	5.64	5.72	5.75	5.75	5.75	5.75	5.75	5.73

<u>Legend</u>: A = After 1 day under 10^{-5}-10^{-4} Torr CO at ambient temperature
B = " 2 days " 10^{-5}-10^{-4} Torr CO " " "
C = " 4 " " 10^{-5}-10^{-4} Torr CO " " "
D = " 16 hours " 10^{-5}-10^{-4} Torr CO " 100°C
E = " 80 " " 10^{-5}-10^{-4} Torr CO " 100°C
F = After pumping and heating at 300°C during 16 hours

work functions calculated from them are given as Φ_{fresh} in Table III. Subsequently, the film was equilibrated by heating the cathode at 300°C. The method of simultaneous evaporation has the advantage that the gold and platinum atoms are brought in each others vicinity. This does not necessarily imply that a metastable solid solution with random distribution

of the atoms is formed, as will be explained in part 4.
But for those compositions outside the miscibility gap where a solid solution is stable, it may be expected that this solution is formed in situ by the present technique and that it will remain almost unaltered. In Fig. 7 a rather pronounced minimum occurs at the gold-rich side at

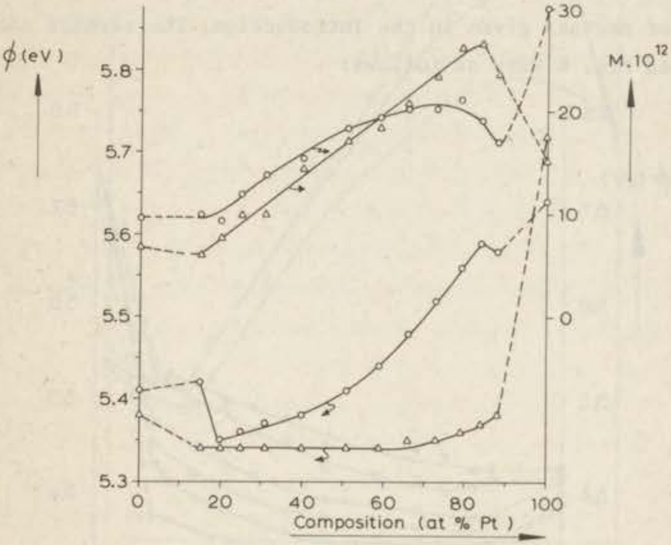


Figure 7

The work functions (lower curves) and the emission constants (upper curves) of a film prepared by simultaneous deposition of the metals (experiment III).

O fresh films

Δ film after sintering at 300°C

about 20 at% Pt, whereas all other values lie on a gradually increasing line from gold to platinum. A small dip in the curve at 90 at% Pt might indicate the in situ presence of an appreciable amount of the stable, platinum-rich composition in the surface area irradiated by the light beam. After sintering at 300°C during two hours the work function of the alloys appear to be located on a plateau having a value of 5.34 - 5.37 eV for a bulk composition from 10 to 90 at% Pt. It is noteworthy that the alloys now possess work functions lower than that of either pure metal and that the value of the plateau coincides with the value of the minimum at 20 at% Pt of the fresh film.

d) <u>Experiment IV</u>: Chemisorption of carbon monoxide

After equilibration of the film of experiment III carbon monoxide was admitted for reasons given in the Introduction. The results shown in Table III and Fig. 8 were as follows:

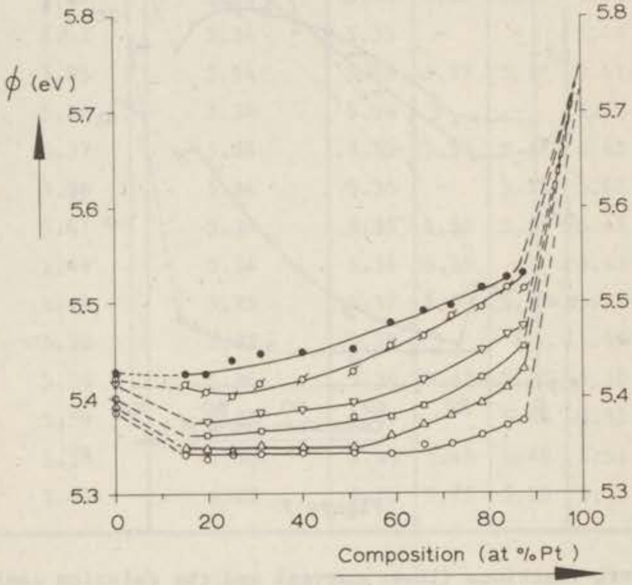


Figure 8

The work functions of an equilibrated alloy film after treatments with CO (experiment IV).

○ film sintered at 300°C

△ after 16 hours exposure to 10^{-4} Torr CO at 20°C

□ " 40 " " " " " " " "

▽ " 90 " " " " " " " "

ø " 16 " " " " " " " 100°C

● " 80 " " " " " " " "

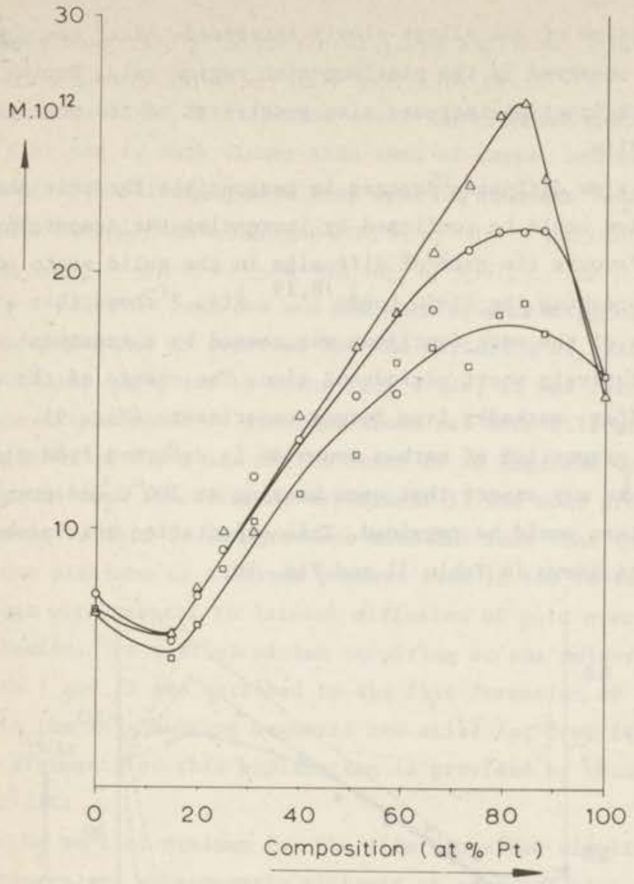


Figure 9

The emission constants of an equilibrated alloy film after treatments with CO (experiment IV).

△ film sintered at 300°C

○ after 90 hours exposure to 10^{-4} Torr CO at 20°C

□ " 80 " " " " " " " 100°C

Immediately after admission of CO, no appreciable change of the work function of gold and the alloys was observed, while Φ_{Pt} was raised by about 0.03 eV. Upon maintaining the film under a pressure of about 10^{-5} - 10^{-4} Torr CO during one day, two days and four days respectively, the work function of all alloys slowly increased. After one day this increase was observed in the platinum-rich region only. During subsequent days, the work function increase also penetrated to the more gold-rich part of the film.

Obviously, a slow diffusion process is responsible for this phenomenon. This conclusion could be confirmed by increasing the temperature to a value which favours the rate of diffusion in the solid state substantially, without breaking the Pt-CO bonds^{18,19}. Fig. 8 shows that a considerable increase of the work functions was caused by a treatment at 100°C during comparatively short periods of time. The change of the emission constants differ markedly from former experiments (Fig. 9).

As the major proportion of carbon monoxide is desorbed from platinum at 300°C^{18,19}, one may expect that upon heating at 300°C and pumping, the original plateau would be regained. This expectation was indeed confirmed by the results shown in Table II and Fig. 10.

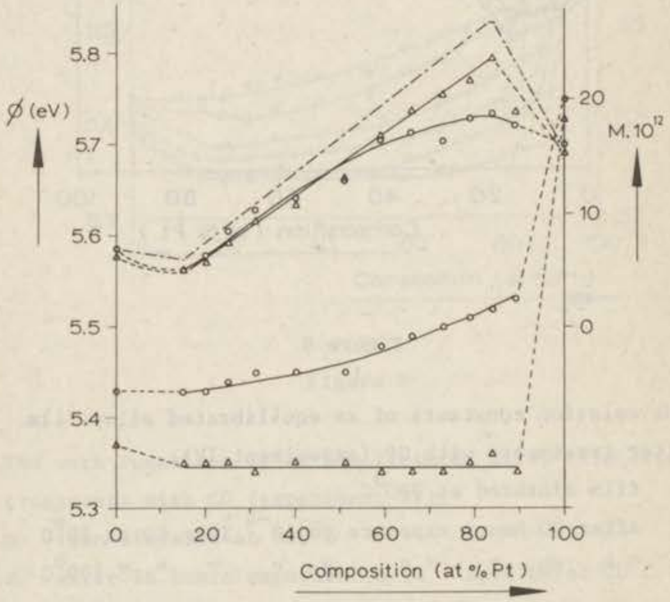


Figure 10

Re-equilibration of the CO-treated alloy film (Experiment IV).

○ final stage of CO-treatment

Δ after pumping at 300°C

4. Discussion

From experiments I and II it became clear that the interdiffusion of gold and platinum is much slower than that of copper and nickel. This is in agreement with diffusion data from Jost[20]. From the well-known relation for the diffusion coefficient D:

$$D = D_o . e^{-Q/RT}$$

wherein $D_o = 1.24.10^{-3}$ cm²/sec and the activation energy of diffusion Q = 39.0 Kcal/g-atom, as reported for the diffusion of platinum in gold between 740° and 986°C and by using Fick's law, it was calculated that the average displacement of platinum atoms per hour will be of the order of one Ångström at 200°C and of the order of 10 Ångström at 300°C. The changes in the work functions of experiment II are more pronounced than in experiment I. This is in agreement with the fact that the diffusion of gold into platinum is a faster process than in the reverse direction. The findings with respect to lateral diffusion of gold over platinum support this conclusion. The partial minima occurring at the gold-rich side for experiments I and II are ascribed to the fast formation of a gold-rich alloy while the neighbouring segments are still far from equilibrium.
A further argument for this explanation is provided by results of experiment III:
In Fig. 7 the partial minimum for the film deposited simultaneously at liquid nitrogen and subsequently sintered at room temperature, lies at about the same level as the plateau of the alloys equilibrated after sintering at 300°C.
It seems, therefore, that the sintered films of experiments I and II were far from equilibrium, while the sintered film of experiment III was equilibrated.

The maximum, shown in Figs 6 and 7 is not representative for all measurements. The peculiar values found near the edges of the photocathode, especially at the platinum-rich side, however, always disappeared after sintering. It seems plausible to assume that premature sintering of segments near the platinum source might cause a local maximum of the work function.
The results from experiment III are in agreement with our stated expec-

tation: the Pt-Au system behaves in a manner analogous to the Ni-Cu system. The kinetic energy of the impinging metal atoms in combination with the lattice energy liberated by each condensing atom and the heat of radiation emitted from the evaporation sources will enable the growing film to acquire an atomic arrangement which is somewhere in between the metastable state of a random distribution and the thermodynamically stable state of two coexisting alloys of different composition.

We visualize that separate clusters of gold-rich and platinum-rich nuclei are formed. The gradually increasing work function from gold-rich alloys up to Pt-rich alloys may be explained by representing a surface containing both platinum and gold in about the same proportions as represented on the abcissa . During sintering an accelerated interdiffusion of the clusters takes place by relatively rapid surface diffusion, migration along the boundaries of neighbouring crystallites and by the relatively slow volume diffusion. Gold having the highest mobility, the lowest surface tension and in relation to platinum, a pronounced Kirkendall effect will diffuse rapidly over the platinum clusters by surface diffusion and grain boundary diffusion.

Our lateral diffusion data are in agreement with this assumption.

After and to some extent during the surface migration of gold, the composite clusters consisting of a platinum kernel and a gold skin, will equilibrate by volume diffusion.

This process comes to an end after formation of the stable gold-rich or platinum-rich alloys. For those compositions where the phase diagram predicts only one single phase rich in platinum, an enrichment of the surface with gold is still possible because in this way the surface energy may be lowered. This follows from the values of the surface tensions which are for gold and platinum 754[21] and 1885[22] dynes/cm respectively (measured at their respective melting points).

Adsorbed carbon monoxide rises the work function of platinum by 0.03 eV. This result is at variance with the contact potential values of Sachtler and Dorgelo[23] (+ 0.23 eV), the field emission data of Rootsaert, Van Reyen and Sachtler[15] (+0.68 eV) and the field emission data of Lewis and Gomer[18] (+ 0.4 eV). Our photoelectric results on pure platinum which will be published[24] more extensively are, however, in reasonable agreement with the static capacitor data of Tompkins and Heyne[25] who reported a change of the surface potential of 0 ± 0.01 eV on polycrystalline platinum films. This small effect of CO on the work function of platinum severely limits the usefulness of CO for chemisorptive titration of platinum-containing gold surfaces.

The result that the work function of our alloys was found unchanged within the experimental error (± 0.005 eV for a single Fowler plot) after short exposition to carbon monoxide gas therefore permits only the semi-quantitative expectation that the platinum content of these surfaces must have been less than about 17at%. The slow phenomena observed after exposition to CO for extended periods of time are, however, remarkable; these may be summarized.

1) The work function slowly increases over a period of days. The highest rate of increase is observed at the most platinum-rich side of the plateau.
2) The emission constants of the alloy change gradually with time (for the sake of clarity, only three curves are shown in Fig. 9).
3) Upon heating at a moderately high temperature (100°C) the effects described in (1) and (2) are accelerated and completed.
4) After heating at 300°C while pumping off the carbon monoxide, the work function of the alloys returnsalmost exactly to their original values and the shape of the emission constant curve changes to its original shape and almost to its original position (Fig. 10).

We interpret these phenomena by assuming that in the presence of CO gas, the alloy surfaces become slowly enriched with platinum, as predicted in the Introduction. Even the shape of the curves in Fig. 8 can be explained in this way. In the platinum-rich region on the photocathode, the crystallites consist of a rather thick platinum-rich kernel surrounded by a thin gold-rich skin, whereas the crystallites in the gold-rich region comprise relatively thick gold-rich jackets around a minor platinum-rich kernel. The path of diffusion, therefore, for Pt-atoms from the kernel to the surface is shorter for the platinum-rich film segments than for the gold-rich side. As soon as a Pt-atom has arrived at the surface a new bond is formed with an impinging CO-molecule preventing diffusion of this Pt-atom back into the interior.

It is obvious that the diffusion process will be faster at higher temperature as was found experimentally.

It may be that the process of thermal diffusion of a Pt-atom from the interior to the surface is accelerated by lattice defects injected into the subsurface zone by the phenomenon of corrosive chemisorption[26]. As the heat of adsorption of CO on platinum[15,16] is at least 30 Kcal. mole^{-1}, the existence of corrosive chemisorption in this case[24] is possible. The behaviour of the emission constant (Fig. 9) indicates that bulk-effects become more involved during the course of the treatment of CO. According to the bulk diffusion data of Jost[20] Pt-atoms can diffuse through gold only over distances of less than 10^{-3} Å/hour at 20°C. As the changes found by us are much faster it is not unlikely that corrosive chemisorption of CO is involved in this process of migration of Pt-atoms from the bulk to the surface.

5. Conclusions

The equilibration model developed on basis of the copper-nickel alloy system, showing a miscibility gap in the solid state is valid also for the platinum-gold system. The model, therefore, appears to be representative for the equilibration of alloys possessing a miscibility gap and being composed of metals having considerably different diffusion rates. The rate of equilibration depends on the temperature and the length of the diffusion path. For the Au-Pt system only simultaneously evaporated alloys were able to reach equilibrium at 300°C within a reasonable period of time. The work function of equilibrated Au-Pt alloys all lie below that of each of the pure metals. This, again, is analogous to the copper-nickel system. Although minima in the work function were reported also for other alloys[27-32], we are unable to say to what extent this phenomenon may be generalized. In the case of K-Na alloys, Van Oirschot[33] did not observe a minimum in the work function. The results further show that the surface composition of an alloy strongly depends on the contacting gas. Chemisorption of carbon monoxide induces a rearrangement of the metal atoms in the equilibrated alloy films, resulting in an increased Pt/Au ratio at the surface. The major proportion of the CO-Pt bonds are broken at 300°C; by pumping CO at that temperature the Pt/Au ratio of the surface returns to the value prior to admission of CO.

Acknowledgements

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

The authors are indebted to Mr. F.C. Kauffeld for skilfully developing and constructing the phototubes.

References

1) W.M.H. Sachtler and G.J.H. Dorgelo, J. Catalysis 4, 654 (1965).

2) W.M.H. Sachtler and R. Jongepier, J. Catalysis 4, 665 (1965).

3) W.M.H. Sachtler, G.J.H. Dorgelo and R. Jongepier, Proc. Int. Symp. Basic Problems Thin Films Phys., Clausthal, 1965.

4) P. van der Plank, Thesis (1968), Leyden University, the Netherlands.

5) P. van der Plank and W.M.H. Sachtler, J. Catalysis 12, 35 (1968).

6) A.A. Vecher and Ya. I. Gerasimov, Russ. J. Phys. Chem. (Engl. Transl.) 37, 254 (1963).

7) R.A. Rapp and F. Maak, Acta Met. 10, 62 (1962).

8) W. Seith and A. Kottmann, Angew. Chemie 64, 379 (1952).

9) G.O. Trønsdal and H. Sørum, Phys. Stat. Sol. 4, 493 (1964).

10) D.A. Cadenhead and N.J. Wagner, J. Phys. Chem. 72, 2775 (1968).

11) A.S. Darling, R.A. Mintern and J.C. Chaston, J. Inst. Met. 81, 125 (1952).

12) L.J. van der Toorn, Thesis (1960), Technical University, Delft, the Netherlands.

13) A. Bolk, Acta Met. 9, 632 (1961).

14) A. Bolk, Acta Met. 9, 643 (1961).

15) W.J.M. Rootsaert, L.L. van Reyen and W.M.H. Sachtler, J. Catalysis 1, 416 (1962).

16) D. Brennan and F.H. Hayes, Phil. Trans. Roy. Soc. A 258, 347 (1965).

17) W.K. Hall, J. Catalysis 6, 314 (1966).

18) R. Lewis and R. Gomer, Suppl. al nuovo Cimento V, 2, 506 (1967).

19) A.E. Morgan and G.A. Somorjai, Surface Science 12, 405 (1968).

20) W. Jost, Z. phys. Chem. B 21, 158 (1933).

21) V.I. Smirnova,and B.F. Ormont, Sh. Fis. Chimii 33, 771 (1959).

22) R. Allen, Trans. AIME 227, 1175 (1963).

23) G.J.H. Dorgelo and W.M.H. Sachtler, Naturwiss. 46, 576 (1959).

24) R. Bouwman, H.P. van Keulen and W.M.H. Sachtler, Ber. Bunsenges. physik. Chem. 74, 198 (1970).

25) H. Heyne and F.C. Tompkins, Proc. Roy. Soc. (London) A 292, 460 (1966).

26) W.M.H. Sachtler, Angew. Chem. internat. Edt. 7, 9 (1968).

27) M.L. Dyubua, O.K. Kultashev and L.V. Gorshkova, Soviet Physics - Solid State 8, 882 (1966).

28) K.P. Gurov and A.I. Pekarev, Fiz. metal. metalloved. 17, 500 (1964)

29) B.C. Dyubua, O.K. Kultashev and I.A. Tsyganova, Radiotekhn. i. ēlektron. 9, 2061 (1964).

30) B.Ya. Pines, Zh. tekhn. fiz. 22, 1908 (1952).

31) B.C. Dyubua and O.K. Kultashev, Fiz. metal. metalloved.21, 396 (1966).

32) B.C. Dyubua, A.I. Pekarev, B.N. Popov and M.A. Tylkina, Radiotekhn. i. ēlektron. 7, 1566 (1962).

33) Th.G.J. van Oirschot, Thesis (1970), Leyden University, the Netherlands.

Chapter VII

INVESTIGATION OF THE SURFACE COMPOSITION OF Ag-Pd ALLOY FILMS

1. Introduction

Binary alloys, which are characterized by a miscibility gap in the solid phase, and which consist of metals having considerably different diffusion rates, can, under certain circumstances, have a constant surface composition, independent of the overall compostion within the miscibility gap of the system.

This phenomenon, which has been proved for Au-Pt[1] and Cu-Ni alloy films[2-4], prepared and sintered in ultra-high vacuum, is of general interest.

The applicability of these alloys in heterogeneous catalysis is however limited as a consequence of the gap of "missing surface compositions".

A phenomenon, first observed with gold-platinum alloys, but not necessarily confined to them, is the change in surface composition, caused by chemisorption of a gas which forms strong bonds with one alloy partner and weak bonds with the other. In this thesis we shall use the term "de-alloying" for this phenomenon.

In view of the results obtained so far on alloys forming a discontinuous series of solid solutions, it is interesting to study also the surface composition of an alloy system forming a continuous series of solid solutions at relatively low temperatures.

From the catalytic point of view, three systems which are believed to be completely miscible at temperatures higher than 300°K, are of interest: silver-palladium[5-8], silver-gold[9] and gold-palladium[10].

The choice of one of these systems has been based on two motives, the first of which is that it should give an opportunity to check the principles of de-alloying and the second, that it should contain interesting prospects with regard to future catalytic experiments on alloys. In this respect, the silver-palladium system is preferable, because

1. Silver is a unique catalyst for the oxidation of ethylene to ethylene-oxide[11] and interesting modifications of activity and selectivity are caused by alloying it with gold[12-14] or palladium[15,16].
2. De-alloying can easily be studied on silver-palladium alloys by using carbon monoxide as the selective adsorbate.

In spite of the integral miscibility of the silver-palladium alloy system the surface composition is not necessarily equal to that of the bulk, for the difference in surface energy between silver and palladium is the thermodynamic driving force for the enrichment of the surface with the metal having the lowest surface energy, viz. silver.

2. Experimental

All experimental details except the evaporation technique of silver and palladium have been given in Chapter VI. Silver was evaporated from tungsten in a similar way as gold, and palladium was evaporated as such in a phototube of type II (see Chapter VI). The alloy films were prepared by simultaneous sublimation of the two metals onto the cathode support which was cooled, at 78°K.

3. Results

a. Sintering phenomena of the pure metal films

The change of the work function Φ and the emission constant M as a function of the temperature of presintering were studied both for silver and palladium, as had been effected for gold, platinum and ruthenium (see Chapter IV).

The results are presented in Table I and Figs. 1 and 2.

The work function of the metals is increased by sintering and constant

TABLE I

The work function Φ (eV) and emission constant M (electrons.photon^{-1}.deg^{-2}) of silver and palladium films as a function of the temperature of presintering T_s.

T_s (°K)	Silver		Palladium	
	Φ	$M.10^{12}$	Φ	$M.10^{12}$
78	4.18	14.2	4.90	38.9
293	4.33	11.4	5.10	51.2
373	4.35	10.8	5.20	39.4
473	4.37	9.8	5.22	37.5
573	4.37	8.6	5.22	31.5

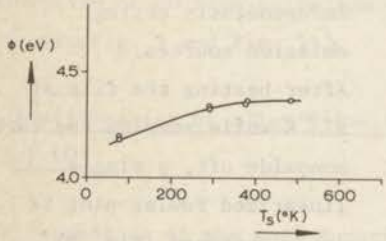


Figure 1

The work function of silver films as a function of the temperature of presintering.

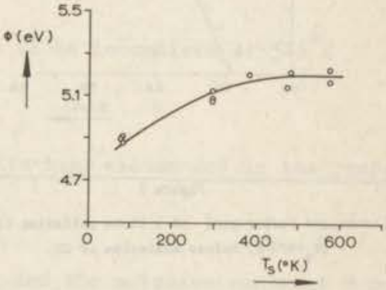


Figure 2

The work function of palladium films as a function of the temperature of presintering.

surface properties are obtained at a sintering temperature which is roughly equal to one-fourth or one-third of the melting point of the metal.

b. Adsorption of CO by the pure metal films

In this case, the study of the adsorption of CO by clean films was restricted to films presintered at 573°K.
On silver, no change of Φ and M was observed after admission of CO up

to a pressure of 10^{-3}Torr. This is in agreement with recent findings by Pritchard[17].

On palladium films however, a behaviour dissentient from that of all other group VIII metals studied so far, was observed. Prior to admission of CO, a linearized Fowler plot can be fitted to all data (Fig. 3).

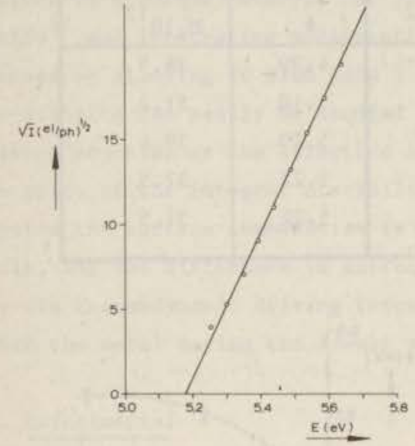


Figure 3

Linearized Fowler plot of a clean palladium film (T_s=573°K) before admission of CO.

Immediately after admission of CO (p = 10^{-4}Torr) the original linearized Fowler plot has changed into a broken line apparently composed by superposition of two straight lines (Fig. 4).

These plots can be analysed[18] yielding two distinct work functions Φ_1 and Φ_2 when we assume that there are two independently acting emission sources.

After heating the film at 573°K while pumping the carbon monoxide off, a single linearized Fowler plot is again obtained (Fig. 5).

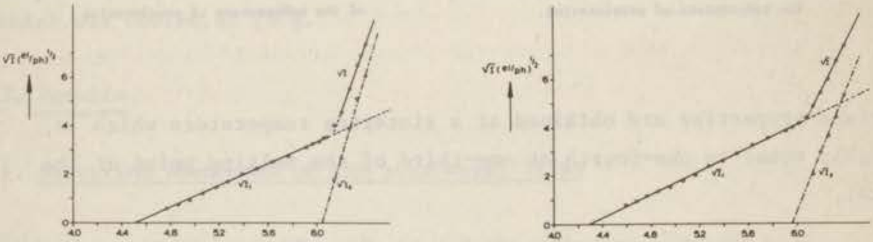


Figure 4a **Figure 4b**

Composite Fowler plots of CO-covered palladium films (T_s=573°K).

4a. T_{ads}= 293°K

4b. T_{ads}= 78 °K

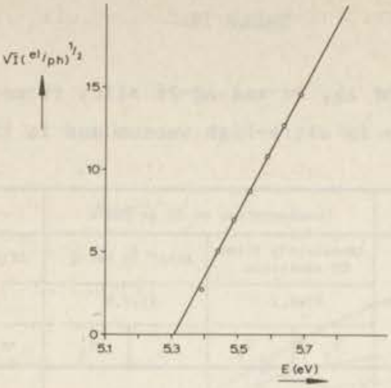


Figure 5

Linearized Fowler plot of a CO-treated palladium film (T_s=573°K) after desorption of CO. at 573 °K

Desorption of CO from palladium seems to be incomplete at 573°K (compare Fig. 3 and Fig. 5).

c. Equilibration of alloy films in ultra-high vacuum and in the presence of CO

The dependence of the work function Φ and the emission constant M on the overall composition is displayed in the Tables II and III and the Figures 6 and 7 for:

1. the freshly vapour-quenched film immediately after sintering at 293°K;
2. the equilibrated film (T_{eq} = 573°K) and
3. the film after admission of CO and after various treatments with CO.

It is noteworthy that after equilibration of the bimetal film by heating at 573°K, a silver-rich surface composition seems to be suggested by the work functions. Even a plateau of the work function can be observed between 53 and 86at% Pd.

Immediately after admission of CO, the work function of all alloys and that of pure palladium are raised. We assume, which will be discussed

TABLE II

The work function Φ of Ag, Pd and Ag-Pd alloy films in the course of successive treatments in ultra-high vacuum and in the presence of CO

Composition x (at% Pd)	Equilibration		Chemisorption of CO at 293°K				– at 373°K		Desorption
			Immediately after CO admission		After 16 hours		After 16 hours		
	T_{eq}=293°K	T_{eq}=573°K	Φ(eV.)		Φ(eV.)		Φ(eV.)		T_{des}=573°K
			Φ_1	Φ_2	Φ_1	Φ_2	Φ_1	Φ_2	
0	4.33	4.38	4.38		4.38		4.38		4.38
10	4.36	4.37	4.46		4.45		4.45		4.37
17	4.36	4.36	4.53		4.45		4.45		4.40
33	4.38	4.44	4.53		4.56		4.50		4.44
53	4.41	4.52	4.78		4.51	4.85	4.51	4.89	4.52
72	4.50	4.50	4.82		4.51	4.90	4.51	5.09	4.52
86	4.87	4.50	4.84		4.51	4.92	4.50	5.18	4.51
100	5.11	5.22	4.50	6.04	4.50	6.04	4.50	6.04	5.33

TABLE III

The emission constant M (electrons.photon^{-1}.deg^{-2}) of Ag, Pd and Ag-Pd alloy films in the course of successive treatments in ultra-high vacuum and in the presence of CO

Composition x (at% Pd)	Equilibration		Chemisorption of CO at 293°K				– at 373°K		Desorption
			Immediately after CO admission		After 16 hours		After 16 hours		
	T_{eq}=293°K	T_{eq}=573°K	$M.10^{12}$		$M.10^{12}$		$M.10^{12}$		T_{des}=573°K
			M_1	M_2	M_1	M_2	M_1	M_2	
0	11.4	9.8	9.8		9.8		9.8		9.8
10	18.8	5.0	6.9		6.2		6.5		6.7
17	23.9	6.0	5.8		5.8		7.4		5.0
33	29.4	4.8	3.8		3.5		3.5		4.7
53	33.4	11.2	12.5		0.25	14.0	0.34	10.4	14.8
72	37.9	22.1	20.8		0.14	20.0	0.09	15.2	22.7
86	42.5	31.6	25.1		0.12	21.4	0.06	17.1	25.1
100	51.9	28.1	0.07	1.17	0.07	1.17	0.07	1.17	23.7

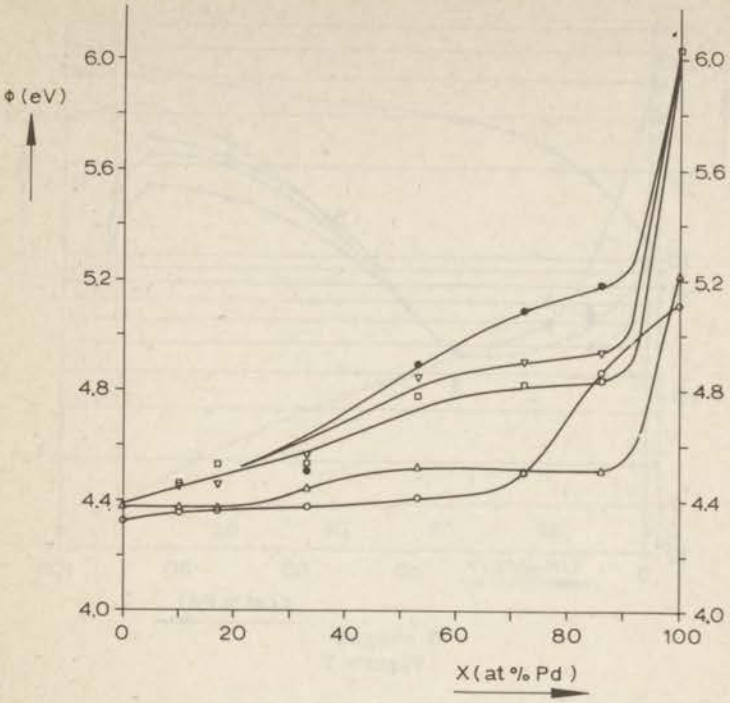


Figure 6

The work function of Ag-Pd alloy films
as a function of the overall composition.

- ○ Freshly evaporated film
- Δ Equilibrated film
- □ Immediately after admission of CO ($p = 10^{-4}$ Torr)
- ∇ After 16 hours exposure to 10^{-4} Torr CO at 293°K
- ● After 16 hours exposure to 10^{-4} Torr CO at 373°K

later, that the highest value Φ_2 of the composite Fowler plot is the "fingerprint" of palladium.

The initial $\Delta\Phi$-values have been plotted as a function of the overall composition in Fig. 8.

From Fig. 8 it appears that the silver content in the surface decreases gradually with increasing palladium content of the bulk.

After exposure to CO at a pressure of 10^{-4} Torr during 16 hours at 293°K

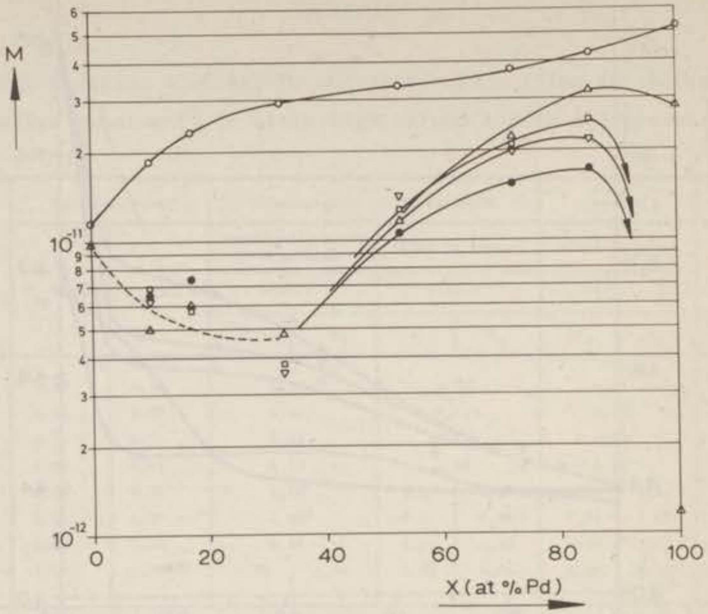


Figure 7

The emission constant of Ag-Pd alloy films as a function of the overall composition.

○ Freshly evaporated film

△ Equilibrated film

□ Immediately after admission of CO ($p = 10^{-4}$ Torr)

▽ After 16 hours exposure to 10^{-4} Torr CO at $293^{\circ}K$

● After 16 hours exposure to 10^{-4} Torr CO at $373^{\circ}K$

the work functions of all alloys with the exception of silver-rich alloys have increased. This effect, which is intensified by heating the film at $373^{\circ}K$ in the presence of CO ($p = 10^{-4}$ Torr), is greater for alloys of higher Pd-content.

Immediately after admission of CO, single linearized Fowler plots were obtained for all alloys. After prolonged treatment with CO at $293^{\circ}K$ and $373^{\circ}K$ single plots were obtained only for alloys containing up to 33at% Pd, whereas alloys richer in palladium yielded composite Fowler plots. For these, the lower value Φ_1 is equal ($\Phi_1 = 4.51 \pm 0.01$ eV) for all

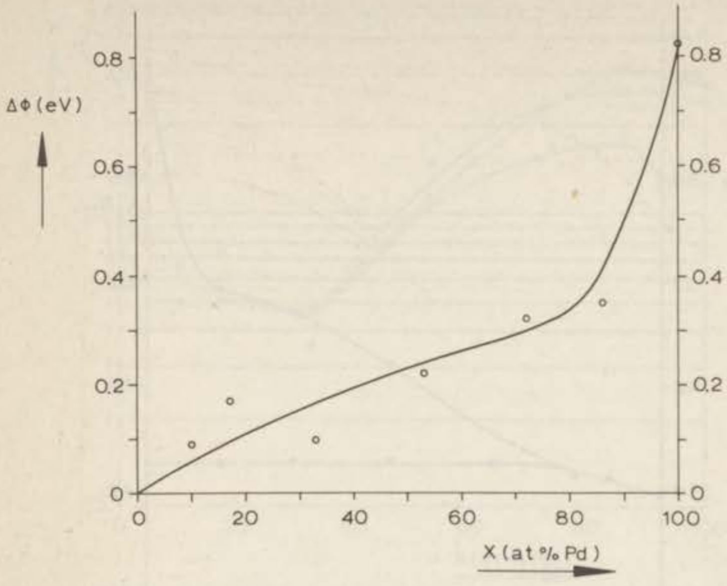


Figure 8

Increase in work function of Ag-Pd alloy films caused by CO-chemisorption as a function of the overall composition.

Pd-rich alloys and for pure palladium, irrespective of the treatments to which the film was subjected, whereas the energy difference between the two characteristic threshold frequencies rises with increasing Pd-content and with prolonged CO-treatment (Fig. 9).
After heating the film at 573°K whilst pumping the carbon monoxide off, the original Φ-vs.-x curve of the freshly equilibrated film is reclaimed, although CO has not been removed completely from pure palladium.

The behaviour of the emission constant M as a function of the overall composition and as a function of the successive treatments is interesting from a phenomenological point of view.
The emission constant of the freshly vapour-quenched alloys after sintering at 293°K exhibits an additive behaviour (Fig. 7).
Sintering at 573°K causes a relatively small reduction of M_{Ag} and M_{Pd}, but remarkable reduction for the emission constant of silver-rich alloys.

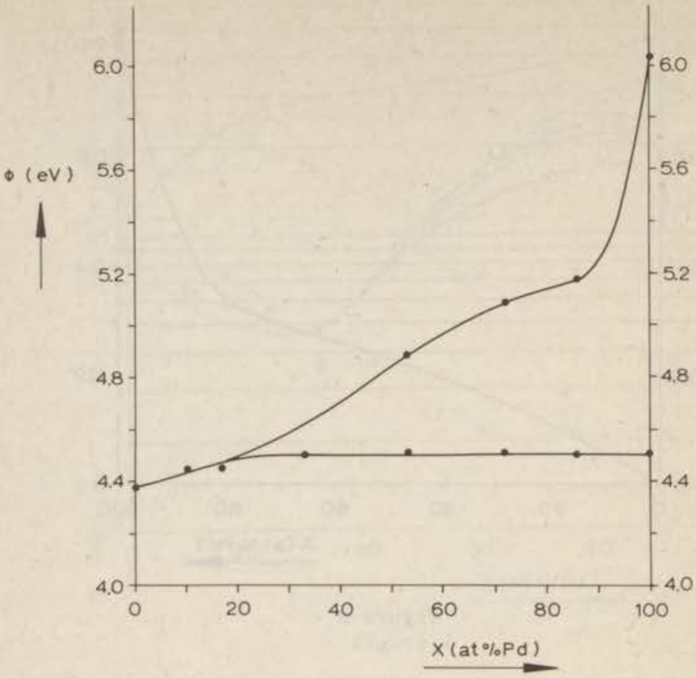


Figure 9

The two work functions Φ_1 and Φ_2 of Ag-Pd alloy films treated with CO ($p = 10^{-4}$ Torr) at 373°K during 16 hours.

M passes through a shallow maximum at about 80-90 at% Pd.
Immediately after admission of CO, M_{Pd} is changed conspicuously while the emission constant of the palladium-rich alloys is affected only moderately. The values of the emission constant for silver-rich alloys present a confusing picture. For palladium-rich alloys, M is further reduced substantially after CO-treatment at 373°K during 16 hours. The change of M, brought about by the CO-treatment , is not appreciable for silver-rich alloys and appears to give no systematic trends.
After desorption of CO by heating at 573°K (Fig. 10), most M-values have increased to almost their original values prior to admission of CO.
From X-ray diffraction measurements, it appeared that the lattice parameters follow Vēgard's law within the experimental error of ± 0.05 at%.

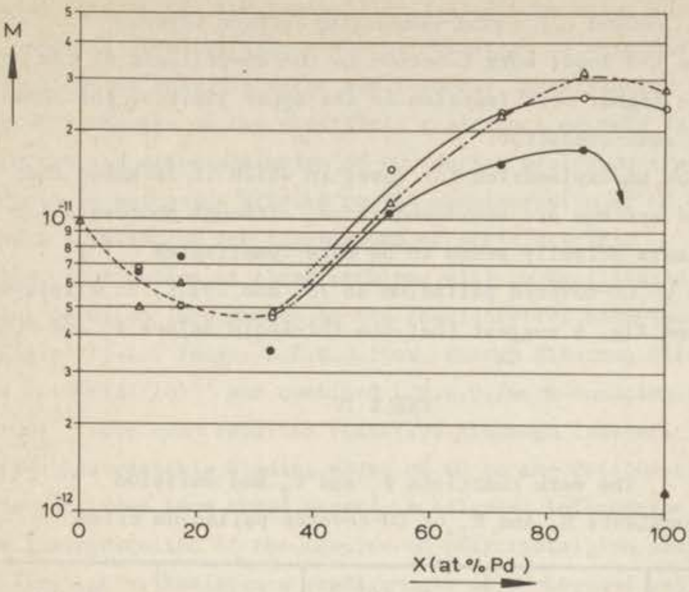


Figure 10

The emission constant of Ag-Pd films as a function of the overall composition before and after desorption of CO.

Δ Freshly equilibrated film

● After 16 hours exposure to 10^{-4} Torr CO at 373°K

○ After desorption of CO at 573°K

4. Discussion

Our previous experience with respect to the equilibration temperature of films having a thickness of 250-500 Å, being roughly equal to $0.3T_m$ (T_m is the melting point of the metal in °K) is supported by results on films of silver, palladium and their alloys.

The spectral distribution of the photoelectric yield of CO-covered palladium is puzzling. So far, no data of this kind have been reported for any group VIII metal covered by CO.

However, similar Fowler plots were reported by Anderson and Klemperer[19] on the oxygen/nickel system and by Suhrmann et al[20] on the oxygen/bismuth system. These authors have interpreted their photoelectric results as having been caused by a semi-conducting surface layer. They ascribe the lower work function to the lower limit of the conduction band and the higher work function to the upper limit of the valence band of the semi-conductor.

This might be an explanation for cases in which it is known that the investigated systems are semi-conductors, although photoemission from semi-conductors actually seems to be more complicated[21,22].

The results on CO-covered palladium at 78° and 293°K, as displayed in Table IV and Fig. 4 suggest that the threshold values Φ_1 and Φ_2 are decreased by cooling. In view of the concept of a semi-conducting surface complex this is surprising as one should rather expect that either no detectable change occurs or a shift to higher threshold frequencies because of the decreased electron population of the accessible levels in the conduction band.

TABLE IV

The work functions Φ_1 and Φ_2 and emission constants M_1 and M_2 of CO-covered palladium films

T_{ads} (°K)	Φ_1	$M_1 . 10^{12}$	Φ_2	$M_2 . 10^{12}$
78	4.30	0.06	5.96	0.54
293	4.50	0.07	6.04	1.17

The decrease of Φ_1 might however be explained by assuming the formation of an electropositive adsorbate of CO.

Another interpretation avoiding the postulate of a semi-conducting surface layer is possible, viz. CO is chemisorbed in such a way that it yields electronegative species on surface-exposed, densely packed, stable crystal planes which, after sintering at 573°K, can be expected to prevail in the surface, whereas it yields electropositive species on other (rough) planes due to, for instance, corrosive chemisorption.

If the patches containing electronegative adsorbate and those containing electropositive species are sufficiently large, electrons can be emitted independently from each patch.

A decision between the two possibilities (semi-conductor surface layer versus specific chemisorption with the formation of extended surface patches) might be possible after simultaneous investigation of photoemission and changes of the electrical resistance of very thin palladium films before and after admission of CO, during prolonged treatment with CO and by extensive studies on the chemisorption of CO by palladium films as a function of the temperature of pre-sintering.

Generally, elucidation of these problems will be facilitated after obtaining detailed information on the chemisorptive behaviour of CO with single crystal faces. L.E.E.D.(Low Energy Electron Diffraction) studies of CO/Pd(110)[23] and combined L.E.E.D./work function studies on CO/Pd(100)[24] have been reported recently. Although isosteric heats of adsorption and possible binding modes of CO on the Pd(110) plane could be concluded from these papers, a balanced information necessary for the interpretation of the results on polycrystalline samples is not yet available. Resistance measurements on CO-covered palladium films reported by Kawasaki et al.[25] can, unfortunately, not be used for the interpretation of the peculiar emission curves of this system, because these authors have studied relatively thick films.

Although the change of the work function of palladium caused by CO adsorption is not as clear-cut a case as that for platinum and ruthenium (see Chapters VI and VIII), there is a fair indication that the highest work function (Φ_2 = 6.04 eV) can be regarded as "fingerprint" for the palladium content in the surface of silver-palladium alloys.

For, upon examining the results from Table I (especially shown in Fig. 9) it is conspicuous that the lower work function is constant (Φ_1 = 4.51 ± 0.01 eV) for <u>all</u> alloys showing composite Fowler plots, irrespective the stage of CO-treatment, while the higher work function Φ_2 increases for palladium-rich alloys. Φ_1 is apparently independent of the silver concentration while Φ_2 is connected with the palladium content. We, therefore, assume that the second work function Φ_2 is indicative for the palladium content of the surface, although we realize that it is not possible to calculate the precise surface composition from the observed $\Delta\Phi$-values. Even the heats of adsorption of CO by Ag-Pd alloys are unknown; it is not out of the question that the heat of adsorption of CO by a Pd-atom which is completely hemmed in by silver atoms is too low for any appreciable chemisorption at the low pressures used in this work. The lower heat of adsorption of CO by Ag-Pd alloys is demonstrated by the desorption experiment (see Table II): after desorption of CO from the film at 573^{o}K, all original Φ-values of the alloys are reclaimed with the exception of that of pure palladium. Recent publications[22,23] provide isosteric heats of adsorption of CO by pure palladium for low coverages, the values being 34 Kcal.mole^{-1} on the (100) plane and about 40 Kcal.mole^{-1} on the (110) plane. It is not unlikely that a small proportion of CO, corresponding with a $\Delta\Phi$-value of about 0.1 eV, remains bound by the less densely packed crystal planes after desorption at 573^{o}K.

Do the experimental results at least permit to decide whether the surface composition of a silver-palladium alloy is enriched with silver or palladium, or equal to that of the bulk ?
For answering this question tentatively, the assumptions are made that every Pd-atom in the surface is capable of adsorbing CO and that the dipole moment of the adsorbed species, in the absence of other adsorbed molecules, is virtually independent of the nature of the surrounding metal atoms. On basis of these assumptions we may visualize that the $\Delta\Phi$-vs.-x curve of the initial CO adsorption experiments has one of the following shapes (see Fig. 11):

1. A straight line connecting the values $(\Delta\Phi)_{Ag}$ = 0.00 eV with $(\Delta\Phi)_{Pd}$= 0.84 eV (curve I). This can be expected if the surface composition is equal to that of the bulk and if there is no mutual depolarization between the adsorbed CO dipoles.
2. A curve representing relatively high $\Delta\Phi$-values (curve II) which will be obtained if the surface is enriched with palladium or if the surface composition is about equal to that of the bulk, but mutual depolarization occurs between the adsorbed CO dipoles.
3. A curve (type III) below curve I: this means that the surface is enriched with silver.

The experimental results follow a curve of type III, so that we may conclude that the surface is enriched with silver. This was in principle to be expected on basis of thermodynamics: silver possesses the lower heat of sublimation and therefore the lowest surface energy .

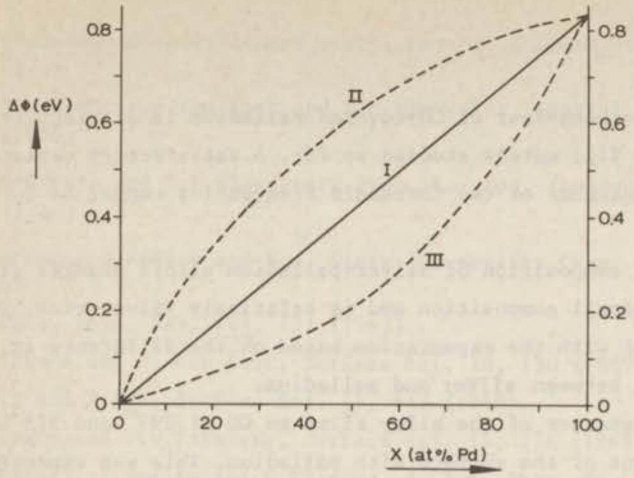


Fig. 11

Possible shapes of the Δφ-vs.-x curve.

The results, presented in Fig.8, also demonstrate that, in contrast with Cu-Ni and Au-Pt alloys, the surface composition of these alloys changes gradually with that of the bulk. Data with reference to the prolonged exposure to CO at 293° and 373°K have made clear that the surface becomes enriched with palladium. This process proceeds with the highest rates for Pd-rich alloys, just as observed for Pt-rich alloys in the case of de-alloying of gold-platinum alloys (chapter VI).
It is unknown whether de-alloying of the silver-palladium alloys proceeds by the creation of vacancies in and below the surface of the film as a consequence of corrosive chemisorption of CO. The mechanism proposed for de-alloying of Au-Pt alloys may also hold for Ag-Pd alloys. But the enhanced mobility of silver and palladium atoms[26] at 373°K can also account for rapid de-alloying without the a-priori necessity of corrosive chemisorption.
As to the emission constant, it appears that this property is too complex to be discussed within the limited experimental context of these investigations. M is therefore treated merely as a phenomenological parameter. It is noted however, that the behaviour of M_{Ag-Pd} resembles the general trends of M_{Au-Pt}.

5. Conclusions

1. The emission behaviour of CO-covered palladium is distinct from all other group VIII metals studied so far. A satisfactory explanation for the appearance of two threshold frequencies cannot be furnished yet.
2. The surface composition of silver-palladium alloys changes gradually with the overall composition and is relatively silver-rich. This is in agreement with the expectation based on the difference in heat of sublimation between silver and palladium.
3. Prolonged exposure of the alloy films to CO at 293° and 373°K results in enrichment of the surface with palladium. This was expected on basis of previous results on gold-platinum alloys. The results on de-alloying of Au-Pt and Ag-Pd alloys support the basic ideas that the surface composition of an alloy in thermodynamic equilibrium depends on the nature of the surrounding gas.

References

1) R.Bouwman and W.M.H.Sachtler, J. Catalysis, in press.
2) W.M.H.Sachtler and G.J.H.Dorgelo, J. Catalysis 4, 654 (1965).
3) W.M.H.Sachtler and R.Jongepier, J. Catalysis 4, 665 (1965).
4) P. van der Plank, Thesis (1968), Leyden University, the Netherlands.
5) J.N.Pratt, Trans. Faraday Soc. 56, 975 (1960).
6) R.Oriano and W.K.Murphy, Acta Met. 10, 879 (1962).
7) K.M.Myles, Acta Met. 13, 109 (1965).
8) J.P.Chan and R.Hultgren, J. Chem. Thermodynamics 1, 45 (1969).
9) J.L.White, R.L.Orr and R.Hultgren, Acta Met. 5, 747 (1959).
10) J.A.Darby, Acta Met 14, 765 (1966).
11) W.M.H.Sachtler, Catalysis Reviews 4, 27 (1970).
12) N.H.A. van Ham, B.E. Nieuwenhuys and W.M.H.Sachtler, J.Catalysis, in press.
13) W.H.Flank and H.C.Beachell, J.Catalysis 8, 316 (1967).
14) T.S.Starostina, A.V.Khasin, G.K.Boreskov and L.M.Pliasova, Doklady Akad. Nauk. S.S.S.R. 190, 394 (1970).
15) R.L.Moss and D.H.Thomas,J.Catalysis 8, 151 (1967).
16) R.L.Moss and D.H.Thomas,J.Catalysis 8, 162 (1967).

17) A.M.Bradshaw and J.Pritchard, Proc. Roy.Soc.(London) Ser A 316, 169 (1970).

18) J.S.Anderson, E.A.Faulkner and D.F.Klemperer, Austral. J. Phys. 12, 469 (1959)

19) J.S.Anderson and D.F.Klemperer, Proc. Roy.Soc. (London) Ser A 258, 350 (1960)

20) R.Suhrmann, G.Wedler and E.A. Dierk, Z. physik. Chem. N.F. 18, 255 (1958)

21) E.O.Kane, Phys. Rev. 127, 131 (1962).

22) J.J.Scheer and J. van Laar, Surface Sci. 18, 130 (1969).

23) G.Ertl and P.Rau, Surface Sci. 15, 443 (1969).

24) J.C.Tracy and P.W.Palmberg, Surface Sci. 14, 274 (1969).

25) K.Kawasaki, T.Sugita and S.Ebisawa, J.Chem. Phys. 44, 2313 (1966).

26) W.Jost, Z.physik. Chem. B21, 158 (1933).

Chapter VIII

INVESTIGATION OF THE SURFACE COMPOSITION OF Pt-Ru ALLOY FILMS

1. Introduction

Catalysis by metals, particularly for hydrogenation reactions is associated with metals having unpaired d-electrons. Platinum and palladium are known as the best, ruthenium as a very poor catalyst for most hydrogenation reactions. It is therefore surprising that a range of alloys of platinum and ruthenium exhibits enhanced catalytic activity above that of the pure metals.

The first reports on this subject, by Amano and Parravano[1] and by Rylander and Cohn[2], deal with various liquid phase hydrogenation reactions.

This phenomenon, called synergism, was first shown for vapour-phase reactions with hydrocarbons by Gray, Masse and Oswin[3].

McKee and Norton[4] showed by means of one of the simplest hydrocarbon reactions, viz. the exchange of protium atoms of methane with deuterium, that a Pt-rich alloy, containing 20 wt% ruthenium, is about ten times as active as pure platinum and more than a thousand times as active as pure ruthenium.

Since then papers appeared repeatedly reporting additional evidence on the synergism of Pt-Ru alloys.

It has now been shown irrefutably that both pure chemical[5-8] and electrochemical[9-13] processes are enhanced by this alloy system more than by either of the pure metals.

This synergism is not restricted to the Pt-Ru system. Early reports by

Nishimura and Taguchi[14,15] on Pt-Rh alloys, prepared according to the Adam's method, show similar trends. Additional studies by McKee[16] and systematic studies by Bond and Webster[17,18] delivered numerous results on various VIII-VIII alloys, all of them showing catalytic synergism.
Up to the present, workers in this field have not yet succeeded in proving unambiguously the reason for this interesting behaviour. The assumption[3] that the presence of one unpaired d-electron would be responsible for optimal activity was disapproved by the spread of maxima, observed on different reactions in the presence of the same alloy catalyst[5].
Also, enhanced activity of reduced oxides of Pt and Pd with respect to the hydrogenation of 1-pentene and nitrobenzene[18] and for the propane hydrogenolysis and the methane-deuterium exchange[19] contradicts the a-priori necessity of one unpaired d-electron for maximal activity. Moreover, it seems to cast doubts on the applicability of the d-band concept as a determining factor for synergism.
In contrast with Au-Pt and Ag-Pd the phase diagram of the Pt-Ru alloy system is unknown, especially at relatively low temperatures, and thermodynamic data are lacking completely. Nemilov and Rudnitsky[20], who studied only part of the system, have shown that these metals form a continuous series of solid solutions within the range 0 - 80at% Ru. These data are slightly at variance with results of Ageev and Kuznetsov[21], who report complete miscibility in the range 0 - 68at% Ru. These studies were performed at high temperatures (e.g. 1,600°C). For catalysts, prepared at low temperatures however, these data are meaningless.
The difference in crystallographic structure* impedes complete solubility at low temperatures. The possible existence of a miscibility gap around 700° - 900°K might have its implications with respect to the surface composition and, hence, to the surface properties of these alloys.
Up to the present, none of the authors who studied this system in catalysis has made an attempt to determine the surface composition of Pt-Ru alloys as a function of their gross composition.
As long as uncertainty exists about the dependence as well in the absence

---

* Platinum has the face centered cubical (f.c.c.) structure and ruthenium the hexagonal close packed (h.c.p.) structure.

as in the presence of an environment which might cause "de-alloying" intricate assumptions on either the electronic or the geometric properties of the surface (lattice parameters[4]) are meaningless for the interpretation of catalytic synergism.

In view of the considerable attention,which is focussed mainly on the Pt-Ru system,and in view of previous results on the equilibration of Cu-Ni[22-24], Ag-Pd and Au-Pt[25] alloys in the absence and in the presence of CO,it seemed highly interesting to get information on the surface composition of equilibrated alloy films of Pt and Ru.
As said before, thin films prepared in ultra-high vacuum are advantageous in this respect,because equilibration of alloy films can be achieved at relatively low temperatures. As shown in chapters III and V, CO is a promising gas for "titrating" the surface composition of Pt-Ru alloys, because the change of the work function of Pt caused by chemisorption of CO[26] is only about +0.05 eV but that of ruthenium[27] is about +0.6 eV, both for highly presintered films. This system, in combination with CO, is also interesting with respect to the phenomenon of "de-alloying". In contrast with Au-Pt and Ag-Pd it consists of two metals, each capable of chemisorbing CO with relatively comparable strength.
For this system we do not expect considerable "de-alloying" caused by prolonged exposure to CO, because the net driving force for one of the metals (namely the one forming strongest bonds with CO) to become enriched in the surface is much lower than in the case of Ag-Pd and Au-Pt.

2. Experimental

General experimental techniques have been described in chapters III, V and VI. On basis of previous results on the equilibration of thin metal and alloy films (chapter IV, 2) the Pt-Ru alloy films can be expected to equilibrate at about 800° - 900°K. The phototube,used for studying this system,is described as tube II in chapter II. This tube was especially designed to study this system, because it enables sintering of the film up to about 1,000°K. Tube II in its present design does not permit simultaneous vapour quenching of the bimetal film. In preliminary experiments composite films were prepared by condensing one metal (e.g. Pt) on top of the previously condensed film (Ru). From X-ray diffraction data it became clear that these two-layer films could not be equilibrated adequately within the temperature limits given by the tube. So the evaporation procedure was changed and all other experiments were carried out on multistratified films consisting of 16 alternating layers of Pt and Ru, having a total thickness of 250 - 500 Å and 1,000 Å near the edges of the photocathode. This means that each individual pure metal layer has a thickness of about 10 atomic layers.

X-ray data from these films indicate complete dissolution of the pure metals into an alloy lattice.

During sintering at 875°K the pressure did not rise above 7.10^{-10} Torr. It is known that CO is a main component of the residual gas in ultrahigh vacuum equipment. To make an estimate of the surface contamination of our films a clean Ru-film was exposed to pure CO ($p = 5.10^{-9}$ Torr), whilst measuring the emission data continuously over an extended period of time. In this way we calculated that the surface contamination of the alloy films, due to chemisorption of CO, is below 1% within the period of sintering. This means, that our results are reliable with respect to surface cleanliness.

Immediately after preparation of the multistratified film, eight positions on the photocathode were investigated. These eight positions were again studied after sintering at 875°K, immediately after admission of CO ($p = 10^{-4}$ Torr) and after exposure to CO ($p = 10^{-4}$ Torr) during 16 hours whilst heating the film at 373°K and 473°K respectively.

3. Results

Relevant results on the work function Φ and the emission constant M are compiled in Tables I and II.

One may observe from Fig. 1 that immediately after preparation of the film an additive behaviour of the work function is detected.

Ruthenium was evaporated first, followed by platinum, which can be observed from the platinum-like behaviour in the range 65 - 100at% Pt. This curve is dotted in Fig. 1, because it reflects only an arbitrary state of the film, which is still far from equilibrium.

After sintering during 16 hours at 875°K, the values have changed and

Table I

The work function Φ(eV) as a function of the overall composition for clean and CO-covered Pt-Ru films

x(at% Pt)	Φ_{fresh}	$\Phi_{eq.}$	$(CO)_{293^{o}K}$	$\Delta\Phi$	$(CO)_{373^{o}K}$	$(CO)_{473^{o}K}$
0	5.08	5.11	5.71	0.60	5.70	5.70
19	5.40	5.13	5.69	0.56	5.69	5.68
33	5.55	5.14	5.66	0.52	5.64	5.66
48	5.62	5.18	5.64	0.46	5.66	5.65
65	5.69	5.30	5.55	0.25	5.55	5.55
79	5.68	5.39	5.55	0.16	5.55	5.54
89	5.72	5.56	5.65	0.09	5.66	5.66
100	5.69	5.71	5.75	0.04	5.74	5.75

Table II

The emission constant M (x 10^{-12}) expressed in electrons.photon^{-1}.deg^{-2} as a function of the overall composition for clean and CO-covered Pt-Ru films

x(at% Pt)	M_{fresh}	$M_{eq.}$	$(CO)_{293^{o}K}$	$(CO)_{373^{o}K}$	$(CO)_{473^{o}K}$
0	12.8	6.0	2.8	2.7	2.7
19	15.3	5.8	2.9	2.8	2.7
33	20.1	6.4	3.8	4.1	4.0
48	19.2	6.9	5.6	5.8	5.5
65	23.6	7.5	6.4	6.2	6.1
79	23.2	7.5	7.2	7.0	6.9
89	26.2	8.9	8.8	8.4	8.5
100	28.0	9.8	10.0	10.2	9.8

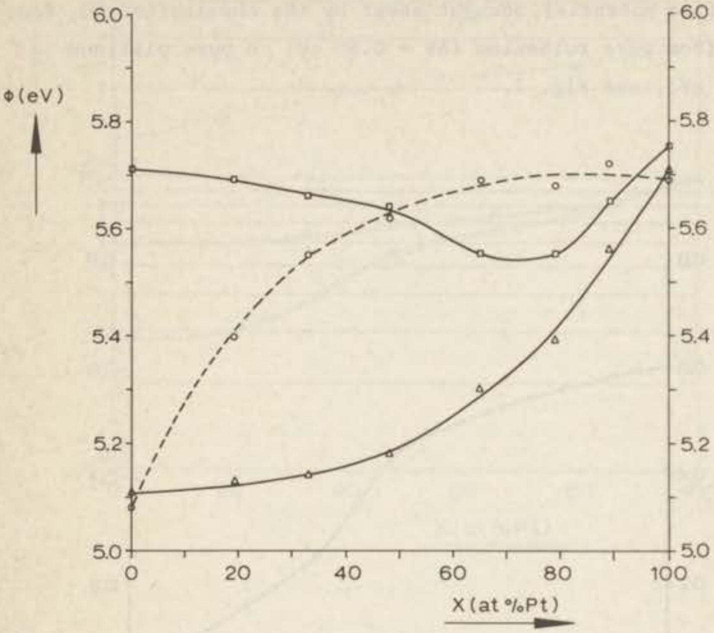


Figure 1

The work function of Pt-Ru alloy films
as a function of the overall composition.
○ freshly evaporated multistratified film
Δ equilibrated film
☐ after admission of CO

again appear to be additive. No minimum of the work function is observed. Repeated sintering did not cause appreciable change of the curves. (These curves were checked only briefly and are not given in Tables I and II). Only the values after the last sintering cycle (after a total of 40 hours) are given in Tables I and II.
From the additive behaviour it is still impossible to draw conclusions on the surface composition of this alloy system,as has already been

pointed out before in chapter I.

After admission of CO an interesting picture emerges. The absolute value of the surface potential, brought about by the chemisorbed CO, decreases gradually from pure ruthenium ($\Delta\Phi$ = 0.60 eV) to pure platinum ($\Delta\Phi$ = 0.04 eV), see Fig. 2.

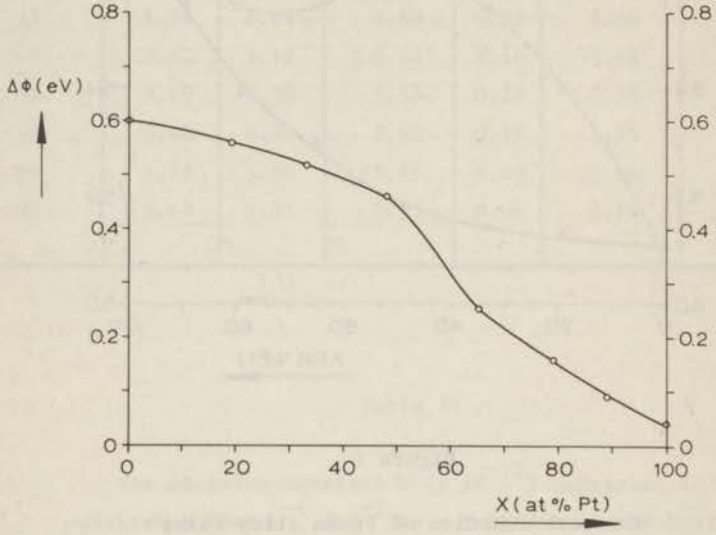


Figure 2

Absolute values of the surface potentials of Pt-Ru films, caused by CO chemisorption, as a function of the overall composition.

The behaviour of the emission constant M is shown in Fig. 3. In contrast with Au-Pt and Ag-Pd the emission constant is an additive function of the composition for the fresh film as well as for the equilibrated and CO covered film.

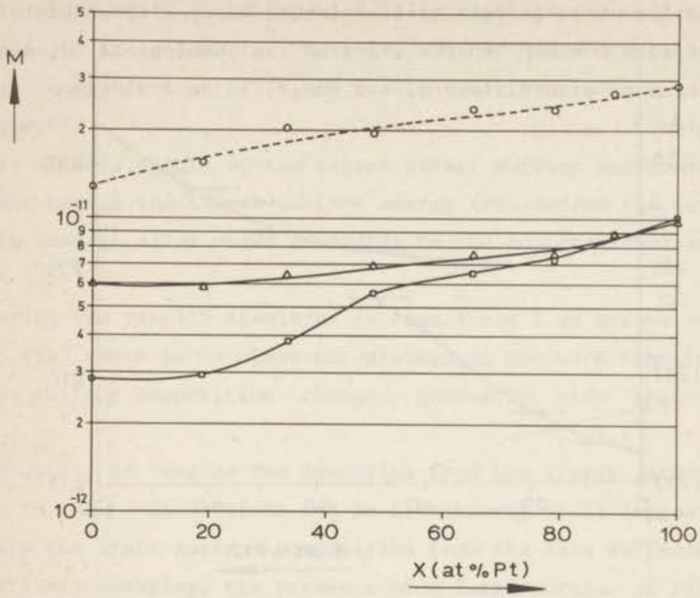


Figure 3

The emission constant of Pt-Ru alloy films
as a function of the overall composition.

○ freshly evaporated multistratified film
Δ equilibrated film
□ after admission of CO

The change in M, brought about by CO chemisorption, is most pronounced on Ru-rich samples and decreases with increasing platinum content.

After prolonged exposure to CO at 373°K and 473°K (see Tables I and II) the work function remains constant within 0.02 eV and the emission constant within $0.4.10^{-12}$ electrons.photon^{-1}.deg^{-2}.

The X-ray diffraction data on this film also yield an interesting picture (Fig.4). As platinum and ruthenium crystallize in different

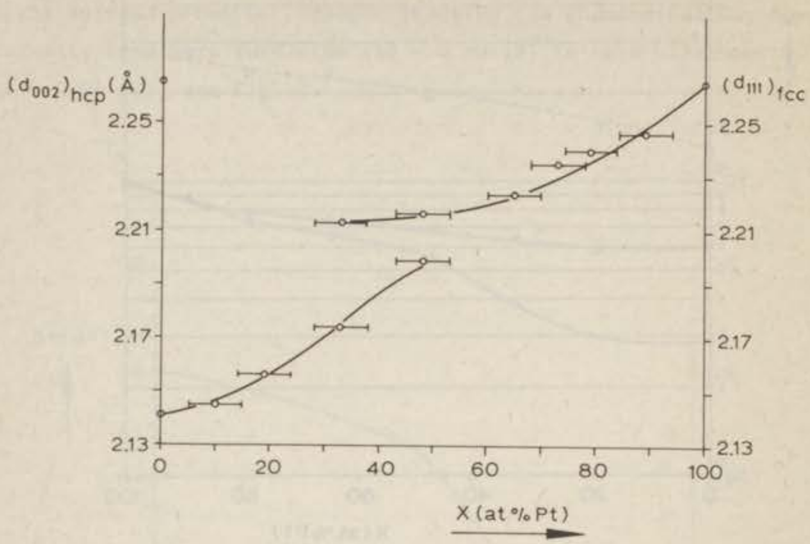


Figure 4

X-ray data of equilibrated Pt-Ru alloy films.

structures, we have used the spacing between the most densely packed crystal planes (d_{111} for Pt and d_{002} for Ru) to obtain an impression on the mutual solubility of the metals. The $(d_{111})_{Pt}$ and $(d_{002})_{Ru}$ data are presented in Fig. 4, which shows that less than 30at% Pt is dissolved in the hexagonal Ru-lattice and less than about 50at% Ru is compatible with the face centred cubical Pt-lattice. In the range 30 - 50at% Pt two phases are present.

4. Discussion and Conclusions

From the work function of the clean, equilibrated films one may observe that neither minima nor maxima are present. So the position of the Fermi level increases smoothly from pure platinum to pure ruthenium.
The X-ray diffraction patterns seem to indicate that Pt and Ru are soluble within each other with the exception of the range 30 - 50 at% Pt.

This result is at variance with McKee's findings, suggesting solubility of up to about 65at% Ru in Pt, which falls right in the middle of our two phase region. It is doubtful however, whether McKee's catalysts which had been homogenized at 573°K, are really equilibrated or metastable solutions.

On basis of this result we can expect either surface enrichment of the component having the lowest surface energy (Pt) and/or the formation of a stable surface alloy phase according to the copper-nickel equilibration model.

Considering the results displayed in Figs. 1 and 2 we arrive at the conclusion that there is no clear-cut plateau of the work function and that the surface composition changes gradually with that of the bulk.

Unfortunately, as long as the deviation from the linear interpolation between the $\Delta\Phi$-values of Pt and Ru is unknown, it is impossible to calculate the exact surface composition from the data reflected in Fig.2. Qualitatively speaking, the presence of a large surplus of Pt in the surface appears unlikely, although some platinum enrichment can be expected from the differences in surface energies of platinum and ruthenium.

A remarkable result is the little response of the Φ-vs-x curve of the freshly CO treated film to prolonged treatment with CO at 373° and 473°K.

From other publications[26,27] it is known that the binding energies between CO and Ru or Pt are roughly comparable.

So, after chemisorption of CO by the metal film, there is insufficient net driving force to enrich one of the metals in the surface. Although this work does not solve the question of synergism on Pt-Ru alloys, it has added information which might be helpful for a better understanding in future. The following remarks with respect to the catalytic behaviour of these alloys can be made:

1. As far as the position of the Fermi level is of importance to catalysis we can now state that it shows no anomalous behaviour.
2. As far as catalysis depends on lattice parameters, we may say with some caution that the lattice parameters are changed gradually from 0 - 30 and 50 - 100at% Pt. In the region 30 - 50at% Pt surface

enrichment of one of the stable phases may prevail in the surface (according to the Cu-Ni equilibration model). It is also possible that the surface contains a plurality of extra specific sites as a consequence of the presence of both f.c.c. and h.c.p. structures. The latter explanation attractive as it may be, would however not be applicable for understanding the catalytic synergism of typical f.c.c. alloys as Pd-Pt, Pt-Ni and Pt-Rh, as reported by Bond[17,18] and McKee[16].

References

1) A. Amano and G. Parravano, Adv. Cat. 9, 716 (1957).

2) R.N. Rylander and G. Cohn, 2nd Int. Congr. Cat. Paris 1, 977 (1960).

3) T.J. Gray, N.G. Masse and H.G. Oswin,- ibid. - 2, 1697 (1960).

4) D.W. McKee and F.J. Norton, J. Phys. Chem. 68, 481 (1964).

5) G.C. Bond and D.E. Webster, Plat. met. Rev. 9, 12 (1965).

6) G.C. Bond and D.E. Webster, Plat. met. Rev. 9, 14 (1965).

7) G.C. Bond and D.E. Webster, Plat. met. Rev. 13, 57 (1969).

8) G.C. Bond and D.E. Webster, Proc. Chim. Soc. (1964) 398.

9) E.W. Brooman and F.P. Hoar, Plat. met. Rev. 9, 122 (1965).

10) J.O.'M. Bockris and H. Wrobloda, J. Elektroanal. Chem. 7, 428 (1964).

11) O.A. Petrii, Dokl. Akad. Nauk. S.S.S.R. 160, 871 (1965).

12) D.V. Sokol'skii, K.K. Dzhardamalieva, A.G. Sarmuzina and T. Tonmarov, Dokl. Akad. Nauk. S.S.S.R. 176, 1093 (1967).

13) D.V. Sokol'skii, A.G. Sarmuzina and K.K. Dzhardamalieva, Tr. Inst. Khim. Nauk, Akad. Nauk. Kazakh. S.S.S.R. 17, 100 (1967).

14) S. Nishimura, Bull. Chem. Soc. Japan 34, 1544 (1961).

15) S. Nishimura and H. Taguchi, Bull. Chem. Soc. Japan 36, 353 (1963).

16) D.W. McKee, a.: J. Catalysis 4, 510 (1965).
b.: Trans. Faraday Soc. 61, 2273 (1965).

17) G.C. Bond and D.E. Webster, Chemistry and Industry 878 (1967).

18) G.C. Bond and D.E. Webster, Plat. met. Rev. 10, 10 (1966).

19) D.W. McKee and F.J. Norton, J. Catalysis 3, 252 (1964).

20) W.A. Nemilov and A.A. Rudnitsky, Izv. Akad. Nauk. S.S.S.R. 1, 33 (1937).

21) N.W. Ageev and V.G. Kuznetsov, - ibid. - 1, 753 (1937).

22) W.M.H. Sachtler and G.J.H. Dorgelo, J. Catalysis 4, 654 (1965).

23) W.M.H. Sachtler and R. Jongepier, - ibid. - 4, 665 (1965).

24) P. van der Plank and W.M.H. Sachtler, J. Catalysis 12, 35 (1968).

25) R. Bouwman and W.M.H. Sachtler, J. Catalysis, in press.

26) R. Bouwman, H.P. van Keulen and W.M.H. Sachtler, Ber. Bunsenges. phys. Chem. 74, 198 (1970).

27) R. Bouwman and W.M.H. Sachtler, unpublished (see chapter V of this thesis).

Chapter IX

GENERAL DISCUSSION

This chapter provides the summarizing discussion on the most important results and the connective text to show the whole study as a coherent system of interconnected parts.

The main objective of this study has been the determination of the surface composition of some alloys as a function of their bulk composition by means of the emission of photoelectrons. This is reflected in the chapters VI, VII and VIII. The four chapters preceeding these provide the preliminary work performed on pure metal films, including the design of specific phototubes so as to solve questions related to the annealing temperature required to equilibrate metal and alloy films, and the chemisorption of carbon monoxide by metal films.

The surface composition of alloys is not necessarily equal to the composition of the bulk in equilibrium.
Generally speaking one may visualize three possible reasons for this deviation:

1. The metals have different surface energy, and surface enrichment by the metal having the lower surface energy is then to be expected[1]. This is, however, counteracted by the misfit of lattice parameters between the enriched surface layer and the underlying alloy lattice.
2. Segregation of an enriched alloy phase according to the Cu-Ni model of Sachtler et al.[2,3]. This requires a miscibility gap in the solid phase and enhanced diffusion rate of one of the metals over the other.

3. Formation of relatively strong bonds between one of the metals with molecules being adsorbed from the surrounding gas. In this case, enrichment by the metal forming the strongest bonds is thermodynamically favourable.

It is not easy to calculate surface enrichment of a completely miscible system (e.g. Ag-Pd) as a consequence of the difference in surface energy between the metals. This is mainly due to the lack of knowledge of the energy required to compress the silver atoms of a silver-enriched surface isotropically so as to match the lattice parameters of the surface with those of the bulk. A completely miscible system like silver-gold seems preferable to check the principle of such a surface enrichment, because these metals have almost the same lattice parameters.

The results on Au-Pt films support the segregation model developed on basis of the Cu-Ni system[3]. Although it may seem obvious that this peculiar type of equilibration can be expected only if the alloy film is equilibrated at a temperature below the critical temperature of mixing, T_c, some authors[4-6] reported results to prove the invalidity of the basic principles of the Cu-Ni segregation model. However, these authors annealed their Cu-Ni films at a temperature above T_c, which was shown to be 322°C according to a recent publication of Kubaschewski[7], so that their results are not relevant for the discussion of the segregation model. It is therefore not surprising,that they find a complete range of solid solutions of copper and nickel: their alloys, equilibrated at temperatures above T_c and studied at room temperature, are evidently frozen in a metastable state of random mixing.
The results on the Au-Pt[8] and Cu-Ni system as obtained by Sachtler et al.[2,3], Van der Plank[9], Cadenhead[10] and Palczewska[11] give a consistent picture. Hence a firm base has been furnished to support the original hypothesis, that the combined action of thermodynamics and kinetics favours the presence of a constant surface composition for bimetal alloys having a miscibility gap in the solid phase and consisting of metals having considerably different diffusion rates so far as the bulk compositions within the miscibility gap, given by the temperature of equilibration,are concerned.

On basis of the Au-Pt and Ag-Pd systems,we have shown that the surface composition of the alloy can be changed by the presence of a gas in contact with the surface. This was, in fact, postulated before[3,12] but never proved experimentally up to the present.

This surface enrichment, denoted as "de-alloying", implies a serious consequence for catalysis by alloys. Until recently, most authors had tacitly assumed that the surface composition of alloys remains unaltered in the course of a catalytic reaction. However, the results displayed in the chapters VI and VII clearly demonstrate that de-alloying can play a rôle. It is a point of discussion whether this phenomenon plays a <u>decisive</u> rôle within the period of laboratory experiments: for it may take too long a time to obtain sufficient surface enrichment to observe a different catalytic behaviour. (In other words , the catalytic surface is not in equilibrium with the bulk of the catalyst and the contacting atmosphere). Moreover, carbonaceous residues, e.g. formed during a reaction involving hydrocarbons, may obstruct the diffusion process in the alloy considerably[13]. However, for commercial catalysts, usually operative for one or more years, the steady-state conditions can possibly be reached during operation and for these catalysts de-alloying can take place.

A recent publication in which the phenomenon of de-alloying is contemplated concerns the oxidation of ethylene to ethylene oxide in the presence of Ag-Pd alloy films[14,15]. The authors report de-alloying in the bulk phase and anticipate silver-enrichment of the surface of Pd-rich samples which they ascribe to the difference in heats of adsorption of oxygen on silver and palladium quoting values of 100 and 50 Kcal.mole^{-1} respectively for silver and palladium.
However, it is doubtful in this case whether silver-enrichment of the surface of the alloy catalyst is due to preferential adsorption of oxygen by silver. Actually, the heat of adsorption of oxygen on silver falls drastically with increasing coverage* to very low values in the order of 10 Kcal.mole^{-1}. The heat of adsorption of oxygen on palladium

---

* For a review on this subject, see ref. (16).

is much higher. Brennan[17] published a value of the integral heat of adsorption on polycrystalline films of 67 Kcal.mole^{-1} and Ertl and Rau[18] reported isosteric heats of adsorption on Pd(110) surfaces varying between 80 Kcal.mole^{-1} at low, and 48 Kcal.mole^{-1} at high coverage. Likewise, the heat of formation[19] of PdO (20.4 Kcal.mole^{-1}) is much higher than that of Ag_2O (6.3 Kcal.mole^{-1}) and Ag_2O_2 (7.60 Kcal.mole^{-1}).

We may expect, therefore, that on the Ag-Pd alloy surface, either

1. The coverage with oxygen is low and the heat of adsorption high, which ipso facto cannot result in a remarkable enrichment of the surface with silver, or
2. The coverage with oxygen is high and the heat of adsorption on the silver atoms is low, so that even enrichment of palladium would be favoured, or
3. The coverage with oxygen is such, that the heats of adsorption of oxygen on silver and palladium are comparable. In that case, no surface enrichment whatsoever is to be expected.

The high mobility of exposed surface metal atoms is demonstrated by several phenomena in this work, viz.

1. The pronounced change of the work function of the pure metals by sintering, mainly at low temperatures (see for instance the results of platinum and ruthenium films between 78° and 293°K, Chapter IV).
2. The results of the chemisorption of CO by Ru-films which suggest that local sintering of non-equilibrated Ru-films is induced by chemisorption of CO (Chapter V).
3. The enhanced diffusion of gold over platinum (Chapter VI).

The high mobility of metal atoms in and near the surface is further demonstrated by the surface enrichment of Pt- and Pd- atoms in resp. Au-Pt and Ag-Pd alloy films during treatments with CO at 293° and 373°K.

These results also have some serious consequences.
Most of the values of the work function of metal films reported hitherto[20,21] have been measured on films prepared and studied under conditions of insufficient surface equilibration. The work function of

metal films should be represented either in the form of a curve as a function of the temperature of presintering, or given as a single value for completely equilibrated films and only the latter value can be used for general purposes, e.g. comparison with other work function values obtained by thermionic emission[22].

The results presented in Chapter V (Chemisorption of CO and adsorption of Xe by ruthenium films) again demonstrate that we must realize that the absolute value of $\Delta\Phi$ is meaningful only when completely equilibrated films are used or when a whole range of films having a different degree of crystallographic disorder is studied.

These results give us opportunity to place a question mark at experimental results on heats of adsorption by non-equilibrated films[23]. The heat liberated by induced sintering of these films, evidently influences the observed heats of adsorption, thus leading to erroneous results if not taken into account. The fact, that the excess free surface energy plays an important rôle has also been recently proved by Sachtler, Kiliszek and Nieuwenhuys[24] who studied the equilibrium reaction:

$$Ni + 4\ CO \rightleftarrows Ni(CO)_4$$

for disordered films and found that the equilibrium constant for this reaction on disordered films is different from that of bulk nickel and interpreted this in a difference of free energy between disordered films and the metal in the standard state.

The value T_s/T_m which seems to be characteristic of surface equilibration is not well defined to exactly 0.3, but it may be used as a "rule of thumb" for predicting the equilibration temperature of a metal film. Experimental results, obtained so far on the equilibration of Cu-Ni, Au-Pt, Ag-Pd and Pt-Ru films having a thickness of 250 - 500 Å, indicate that this rule is also applicable to the equilibration of thin alloy films; the temperature of equilibration in these cases lies between about 0.3 T_m of one metal and 0.3 T_m of the other metal of the alloy. Interesting additional evidence for the equilibration of Au-Pt alloy films (not presented in Chapter VI) is shown in Fig. 1. These results demonstrate that, while heating the film at 373°K and 473°K is evidently insufficient for equilibration, sintering at 573°K produces the plateau discussed in Chapter VI. Prolonged heating at 573°K does not cause any

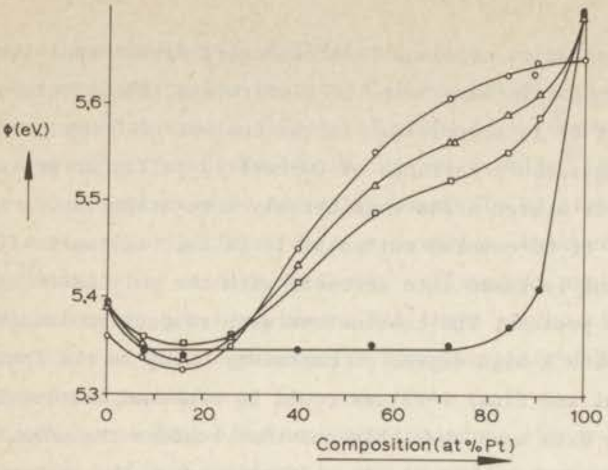


Figure 1

The work function of Au-Pt alloy films
as a function of the overall composition.

○ Freshly evaporated film
Δ After sintering at 373°K
□ After sintering at 473°K
● After sintering at 573°K

additional changes of the Φ-vs.-x curve, while X-ray diffraction data suggest complete dissolution of the metals in alloy compositions. On reflection, the applicability of this rule to thin alloy films evaporated on cooled supports, is not surprising. These films possess a high proportion of surface exposed metal atoms. Hence we may expect, that surface rearrangements will play an important rôle in the equilibration process.

The change of the work function of platinum and ruthenium, brought about by CO-chemisorption, was measured in extenso because data from literature were either lacking, conflicting, or performed by methods differing so principally from photoemission that the results could not be compared easily. In the case of CO/Pt, agreement was reached on the static capacitor measurements on polycrystalline Pt-films by Heyne and Tompkins[25].

We found two adsorption complexes with opposite dipole and ascribe the second "electropositive adsorbate" to a corrosive chemisorption.

The low value of $\Delta\Phi$ is surprising in the context of other group VIII metals[26]. The emission properties of CO-covered palladium are even more puzzling and this system needs considerably more attention.

The value of $\Delta\Phi$ of CO-covered ruthenium is in fair agreement (if no induced sintering is taken into account) with the only other value[27] known up to the present. The conclusions with respect to induced sintering could be made with a high degree of certainty owing to the fact that not only the initial and final Φ-values could be measured absolutely, but that also xenon data were available and that besides the work function the emission constant was available.. In this case, the photoelectric technique of work function measurements has proved to be superior to other techniques. The adsorption study of xenon with ruthenium films has added interesting information. First, it helped to solve the problem of local sintering of the Ru-films. Secondly, it has furnished data which were not known before and thirdly, it has proved that the binding character of xenon on ruthenium comprises more intricate interaction between the metal and the gas than merely that by Van der Waals-London dispersion forces[28].

Another interesting feature of this study is the value of the work function of equilibrated alloy films of gold and platinum. These alloys are characterized by a lower work function than that of the pure metals. This phenomenon has also been reported for systems like Th-W[29,31], Cs-W[30], Th-Re[31], Mo-W[32], Ta-W[32], Hf-W[33,34], Ti-Re[35], Na-Pb[36], Cs-Hg[37], and Cu-Ni[2,3]. Most of these studies have been performed by thermionic emission. Up to present, there is no general agreement on the interpretation of this phenomenon. Lazarev[36,37] who correlates the work function with the surface tension of the alloys in the molten state, proposes that the minima of the work function of Na-Pb and Cs-Hg alloys are found for stable compounds (respectively NaPb and $CsHg_2$).

Dyubua[33] explains the reduction of Φ_W after the addition of hafnium by an increase of the lattice constant of the bulk (a typical volume effect), while Gurov and Pekarev[34] explain these results as being a consequence of a change in the kinetic and potential energy of the free electron gas due to a change in the conduction electron density and the appearance of excess charge at Hf-atoms.

Dyubua[35] later explains the reduction of Φ_{Re} after the addition of titanium by assuming that a film of adsorbed Ti is formed on the Re-Ti alloy (a typical surface effect). His recent results[32] on W-Ta and W-Mo alloys are also explained by assuming adsorption of the lower melting compound on the alloy surface. This explanation, however, apparently does not fit with his results on Ta-Nb[35] alloys. An explanation for the Cu-Ni alloys has not yet been given. All these explanations so far are characterized by a rather qualitative approach without furnishing an unambiguous interpretation.

Notwithstanding the lack of electronic theory on alloys which might give an explanation for this problem, we may visualize two possible causes for the minimum of the work function of Au-Pt alloys:

1. Adsorption of gold as an electropositive adsorbate, by platinum, in line with the explanation of Dyubua[32].

   In our case, however, we have results available which simulate this situation. The monolayer experiment, described briefly in Chapter II, demonstrates that the work function of a platinum film, covered by a monolayer of gold, is that of gold. Also results of Ni-films, covered with fractions of monolayers up to a monolayer of copper, proved[2] that intermediate values between those of Cu and Ni are detected. This explanation therefore seems unlikely for the system gold-platinum.

2. Strain in the surface lattice as a consequence of the misfit between the stable gold-rich alloy surface skin and the underlying platinum-rich kernel.

   However, if this were true, one might expect different Φ-values of the equilibrated alloys in gold-rich and platinum-rich regions, because the gold-rich surface of gold-rich samples is not, or but hardly, subject to strain.

   Moreover, the in-situ minimum at gold-rich side of the photocathode (see this chapter, Fig. 1 and Chapter VI, Fig. 7) represents the stable gold-rich alloy having the same surface and bulk composition and therefore excludes the influence of lattice strain in this particular case.

So, it seems that none of the above-mentioned hypotheses, proposed for rationalizing the minimum of the work function, can withstand critical examination. We are therefore not able to give a satisfactory explanation for this phenomenon without further knowledge of the theoretical background.

In summarizing, this study has lead us to the following conclusions:

1. The surface composition of alloy films is not necessarily equal to that of the bulk. This has been most convincingly demonstrated by means of the gold-platinum system.
2. Gold-platinum alloys equilibrate according to the Cu-Ni model proposed by Sachtler et al.[2,3], thus giving a firm base to the general applicability of the segregation model to other alloy systems obeying the same prerequisites, namely the existence of a miscibility gap and the difference in diffusion rates of the metals.
3. The surface composition of Ag-Pd and Pt-Ru alloys is changed gradually with that of the bulk. This has been most convincingly observed for Pt-Ru alloys. The latter have a small miscibility gap (at 875°K) which lies at least between 30 and 50at% Pt.
4. Chemisorption of CO by Au-Pt and Ag-Pd alloys causes "de-alloying" of these alloys, resulting in an enrichment of the surface with the metal which forms the strongest bond with the contacting gas (Pt and Pd respectively).
5. Chemisorption of CO by disordered ruthenium films causes a local sintering of the film. The change of the work function of completely equilibrated Ru-films due to CO-chemisorption is + 0.6 eV.
6. Chemisorption of CO by platinum films[38] leads to the formation of two discernable adsorption complexes with opposite dipoles. The electropositive adsorbate occurs most pronouncedly on disordered films and is ascribed to corrosive chemisorption. The net effect of the two chemisorption complexes for the change of the work function is negligibly small in comparison with other group VIII metals.
7. The work function of a metal film is characterized by one of the following ways: As a function of the temperature of presintering up to the equilibration temperature, which is roughly from one-fourth

to one-third of the absolute melting point of the metal, or by its value after having been sintered at that temperature.

8. The work function of ruthenium has been given in the form of a complete sintercurve[22] and is 5.10 ± 0.05 eV for films sintered at above about 800°K.

References

1) J.L. Meijering, Acta Met. 14, 251 (1966).
2) W.M.H.Sachtler and G.J.H. Dorgelo, J.Catalysis 4, 654 (1965).
3) W.M.H.Sachtler and R.Jongepier, J.Catalysis 4, 665 (1965).
4) J.J. Byrne and J.K.A. Clarke, J.Catalysis 9, 166 (1967).
5) R.S. Mann and K.C. Khulbe, Can. J. Chem. 46, 623 (1968).
6) W.A. Hardy and J.W.Linnett, Trans Faraday Soc. 66, 447 (1970).
7) L. Elford, F.Müller and O. Kubaschewski, Ber. Bunsenges. physik. Chem. 73, 601 (1969).
8) R.Bouwman and W.M.H. Sachtler, J.Catalysis in press.
9) P. van der Plank and W.M.H. Sachtler, J.Catalysis 12, 35 (1968).
10) D.A. Cadenhead and N.J. Wagner, J. Phys. Chem. 72, 2775 (1968).
11) W. Palczewska and S. Majchrzak, Bull. Acad. Pol. Sc. 17, 681 (1969).
12) W.K. Hall, J. Catalysis 6, 314 (1966).
13) A.A. de Keijzer, Thesis (1970), Technical University, Delft, the Netherlands.
14) R.L. Moss and D.H. Thomas, J. Catalysis 8, 151 (1967).
15) R.L. Moss and D.H. Thomas, J. Catalysis 8, 162 (1967).
16) W.M.H. Sachtler, Catalysis Reviews 4, 27 (1970).
17) D. Brennan, D.O. Hayward and B.M.W. Trapnell, Proc. Roy. Soc. (London) Ser.A 256, 81 (1960).
18) G. Ertl and P. Rau, Surface Sci. 15, 443 (1969).
19) National Bureau of Standards, Circular 500, "Selected values of Chemical thermodynamic properties", issued Febr. 1, 1952.
20) R. Suhrmann and G. Wedler, Z. angew. Physik 14, 70 (1962).
21) J.C. Rivière in "The Solid State Surface Science" , Dekker, N. York (1969), p. 179.
22) R. Bouwman and W.M.H. Sachtler, Surface Sci. in press.
23) D. Brennan and M.J. Graham, Disc. Faraday Soc. 41, 95 (1966).
24) W.M.H. Sachtler, C.R. Kiliszek and B.E. Nieuwenhuys, Thin Solid Films 2, 43 (1968).

25) H. Heyne and F.C. Tompkins, Proc. Roy. Soc. (London), Ser.A 292, 460 (1966).

26) A. Eberhagen, Fortschr. Physik 8, 245 (1960).

27) R. Klein, Surface Sci. 20, 1 (1970).

28) Th. G. J. van Oirschot and W.M.H. Sachtler, Proceedings of the "Solid-Vacuum Interphase",Symposium, (1970), Groningen, the Netherlands, in press.

29) W.H. Britain and J.H. Becker, Phys. Rev. 43, 428 (1933).

30) J.B. Tailor and I. Langmuir, Phys. Rev. 44, 423 (1933).

31) J. Anderson, W.E. Danforth and A.J. Williams, J. appl. Phys. 34, 2260 (1963).

32) B.Ch. Dyubua, O.K. Kultashev and L.V. Gorshkova, Sov. Physics-Solid State 8, 882 (1966).

33) B.Ch. Dyubua, A.I. Pekarev, B.N. Popov and M.A. Tylkina, Radiotekhn, i. ēlektron. 7, 1566 (1962).

34) K.P. Gurov and A.I. Pekarev, F.M.M. 17, 500 (1964).

35) B.Ch. Dyubua, O.K. Kultashev and I.A. Tsyganova, Radiotekhn. i. ēlektron. 9, 2061 (1964).

36) V.B. Lazarev and Yu.I. Malov, Elektrokhimiya 4, 662 (1968)

37) V.B. Lazarev, Yu.I. Malov and G.A. Sharpatuya, Dokl. Akad. Nauk S.S.S.R. 178, 355 (1968).

38) R.Bouwman, H.P. van Keulen and W.M.H. Sachtler, Ber. Bunsenges. physik. Chem. 74, 198 (1970).

SUMMARY

The surface composition of three alloy systems, viz. Au-Pt, Ag-Pd and Pt-Ru, have been determined by measuring the photoelectric work function of the clean metals and that of the alloys and the change of the work function, brought about by chemisorption of carbon monoxide.

The metals and alloys have been studied as thin films, prepared by sublimation under ultra-high vacuum conditions (10^{-10} Torr or less).

This thesis consists of three parts:

The first (Chapter II) describes two phototubes, which were especially designed to match the problems, resulting from the nature of the investigated systems. With these tubes, thin films which are prepared and sintered between 78° and 925°K in ultra-high vacuum can be studied. One of them contains as its essential feature a bakeable all-quartz cathode support, which is completely exposed to ultra-high vacuum, and thus permits heating the metal and alloy films at temperatures sufficiently high to equilibrate all the systems under study.

The second part (Chapters III-V) deals with the preliminary work, performed on metal films, especially platinum and ruthenium films, in order to obtain basic information on the work function of ruthenium films, which was unknown hitherto, on the change of the work function of platinum and ruthenium films, caused by CO adsorption, and on the equilibration temperature of metal and alloy films.

In chapter III it is shown that CO is chemisorbed by platinum in two distinguishable complexes, having opposite dipoles. The second, electropositive, adsorbate appears predominantly on disordered films and vanishes with increased ordering of the film. These results have been interpreted in such a manner that both chemi-adsorption, with the

formation of electronegative adsorbate, and corrosive chemisorption, with the formation of electropositive adsorbate, occur. The net effect of these chemisorption complexes on the work function Φ is low (about + 0.05 eV) considered in the context of other group VIII metals.

In chapter IV, the work function of ruthenium films is presented as a function of the temperature of sintering, T_s. Φ_{Ru} is raised with T_s and ceases to increase at $T_s \cong 0.3\ T_m$ (T_m is the melting point of the metal in ^{o}K). This relation, which also holds good for silver, gold, platinum and palladium, seems to be of general validity.

Bimetal alloy films, prepared by simultaneous vapour-quenching at 78^{o}K, are equilibrated at a temperature which is roughly between one-third of the melting points of the two metals.

Chapter V describes work on the change of the work function of ruthenium films, brought about by the adsorption of xenon and carbon monoxide as a function of T_s. For CO, $\Delta\Phi$ is equal to + 1.44 eV for films, vapour-quenched and sintered at 78^{o}K. $\Delta\Phi$ decreases with increasing T_s and is about + 0.6 eV for highly sintered ruthenium films, while the final values of the work function and emission constant of the CO-covered films is about the same, irrespective of the value of T_s between 78^{o} and 473^{o}K. The value of the surface potential, brought about by the adsorption of xenon, is 0.95 $\pm$ 0.05 eV and independent of T_s between 78^{o} and 573^{o}K. These results have been interpreted by assuming that the heat, liberated in the chemisorption of CO, causes a local sintering of initially imperfect ruthenium films.

The third part of this work comprises studies on the surface composition of gold-platinum, silver-palladium and platinum-ruthenium alloy films. The gold-platinum system (Chapter VI) was studied to check the principles of the segregation model developed on basis of copper-nickel alloys. It has indeed been found, that Au-Pt alloy films equilibrate in such a way that a gold-rich stable composition forms the vacuum-exposed surface phase. The gold-rich alloy phase has the same composition for all alloys having overall compositions within the miscibility gap of the system at the temperature of equilibration. For this system it has been proved that the surface of the gold-rich surface phase becomes enriched with platinum as a consequence of prolonged exposure to CO. This phenomenon has been called "de-alloying" in chapter VII. This process is detectable within a period of days at room temperature. Heating at 573°K and pumping the CO off, causes the film to regain its original gold-rich surface composition. These phenomena are in agreement with thermodynamic data. The mechanism of metal atom migration is explained by assuming that CO is chemisorbed corrosively by the alloy, thereby creating vacancies in and adjacent to the surface of the film. As a result, Pt-atoms can diffuse easier from the bulk to the surface.

The work function of clean, equilibrated Au-Pt alloys is lower than that of pure gold and platinum. This phenomenon, which is discussed further in chapter IX, is not yet explicable.

In chapter VII, results are presented of the silver-palladium system. This system was chosen to determine the surface composition of an alloy system, which forms a continuous series of solid solutions at the temperature of equilibration, and to check the phenomenon of "de-alloying". It was found that the surface composition of these alloys is relatively silver-rich, but changes with that of the bulk. The silver-enrichment of the surface of the clean alloys can be explained on basis of the difference between the surface energy of silver and that of palladium. The work function of these alloys is intermediate to those of the pure metals. After prolonged exposure to CO at 293° and 373°K, the surface composition of the Pd-rich alloys becomes enriched with palladium, which was to be expected on basis of the difference between the bond strengths of silver and palladium with CO.

The spectral distribution curve of the photoelectric yield of CO-covered palladium is different from all other group VIII metals, known so far, and is not yet explicable.

Results presented in chapter VIII concern the surface composition of platinum-ruthenium alloy films.

The aim of this study was to reveal the surface composition as a function of the bulk composition, as a first step to understand the catalytic synergism of these alloys, reported repeatedly in relation to hydrogenation reactions.

It was found that Pt-Ru films, equilibrated at 875°K, possess surface compositions which are roughly equal to those of the bulk. The work function of the pure alloys is intermediate to that of platinum and ruthenium.

Ruthenium is compatible with the f.c.c. lattice of platinum up to an amount of about 50 at%. Up to about 30 at% platinum is taken up in the h.c.p. lattice of ruthenium. In the range 30-50 at% Pt, there are two coexisting phases as is proved by X-ray diffraction measurements.
Prolonged exposure to CO does not cause a measurable change in the surface composition within days at 373^{o} and 473^{o}K. This is again in agreement with thermodynamic data, which show that the bond strengths of CO with platinum or ruthenium are comparable.
A general discussion on the most important aspects of this study and possible implications for surface science, is given in chapter IX.

SAMENVATTING

De oppervlaktesamenstelling van drie legeringssystemen, te weten Au-Pt, Ag-Pd en Pt-Ru werd onderzocht door de uittreearbeid Φ en de fotoelectrische emissieconstante M, alsmede de verandering van de uittreearbeid t.g.v. de chemisorptie van CO te meten.

De metalen en legeringen werden bestudeerd in de vorm van dunne films, verkregen door opdampen in ultrahoogvacuüm (10^{-10} Torr of minder).

Dit proefschrift bestaat uit drie delen:

In het eerste deel (Hoofdstuk II) worden twee fotocellen beschreven, speciaal geconstrueerd voor de drie systemen. Hiermee kunnen dunne films welke tussen 78° en 925°K in ultrahoogvacuüm bereid en getemperd zijn, bestudeerd worden. Eén dezer cellen wordt gekarakteriseerd door een uitstookbare, geheel in ultrahoogvacuüm geplaatste, kathodedrager van kwarts. Met deze cel kunnen metaal- en legeringsfilms voldoende hoog verhit worden om de genoemde systemen tot thermodynamisch evenwicht te brengen.

Het tweede deel (Hoofdstukken III-V) heeft betrekking op het voorbereidende werk, dat aan enkele metalen, met name platina en ruthenium, verricht werd. Het doel hiervan was gegevens te verzamelen omtrent de uittreearbeid van ruthenium films, die tot dan nog onbekend was, de verandering van de uittreearbeid, ΔΦ , van platina en ruthenium als gevolg van de adsorptie van koolmonoxyde, alsmede de temperatuur, welke vereist is om dunne metaal- en legeringsfilms tot thermodynamisch evenwicht te brengen. In hoofdstuk III wordt aangetoond, dat CO door platina geadsorbeerd wordt in de vorm van twee onderscheidbare adsorptiecomplexen met tegengestelde dipoolmomenten. Het tweede, electropositieve complex neemt in betekenis af naarmate de kristallografische ordening van de film toeneemt. Deze resultaten werden geinterpreteerd door te veronderstellen dat zowel chemi-adsorptie, gepaard gaande met de vorming van electronegatief adsorbaat, als corrosieve chemisorptie, gepaard gaande met de vorming van electropositief adsorbaat, voorkomen. Het totale effect van beide chemisorptiecomplexen op Φ is zeer klein (ongeveer + 0,05 eV) t.o.v. dat bij andere metalen uit de 8^e groep van het periodieke systeem der elementen.

In hoofdstuk IV is de uittreearbeid van rutheniumfilms gegeven als functie van de temperatuur van voorafgaand temperen (T_s). Φ_{Ru} stijgt met T_s en bereikt een stabiele waarde van 5,10 ± 0,05 eV bij $T_s \cong 0,3\ T_m$ (T_m is het smeltpunt van het metaal in ^oK). Deze vergelijking, die ook opgaat voor zilver, goud, palladium en platina, lijkt algemene geldigheid te hebben. Legeringsfilms, bereid door gelijktijdig opdampen op een tot 78^oK gekoeld substraat kunnen tot evenwicht gebracht worden door verhitting bij een temperatuur, die ligt tussen circa één-derde van de respectievelijke smeltpunten der beide metalen.

Hoofdstuk V verschaft informatie over de verandering van de uittreearbeid van rutheniumfilms t.g.v. de adsorptie van xenon en koolmonoxyde, als functie van T_s. Bij adsorptie van CO op films, bij 78^oK opgedampt en getemperd, is $\Delta\Phi = + 1,44$ eV. $\Delta\Phi$ daalt met toenemende T_s en bereikt een waarde van ca. + 0,6 eV voor volledig getemperde films. De eindwaarden van Φ_{Ru-CO} en M_{Ru-CO} ondergaan geen verandering als functie van T_s tussen 78^o en 473^oK.

De waarde van $-\Delta\Phi$ t.g.v. de adsorptie van xenon door rutheniumfilms is 0,95 ± 0,05 eV en is onafhankelijk van T_s tussen 78^o en 573^oK.

Deze resultaten konden geinterpreteerd worden door aan te nemen, dat de bij de chemisorptie van CO vrijkomende adsorptiewarmte het plaatselijk ordenen van aanvankelijk ruwe rutheniumfilms veroorzaakt.

Het derde deel van dit proefschrift omvat de onderzoekingen naar de oppervlaktesamenstellingen van Au-Pt, Ag-Pd en Pt-Ru legeringsfilms.

Het goud-platina systeem (Hoofdstuk VI) werd onderzocht om het te toetsen aan de beginselen van het fasenscheidingsmodel, dat naar aanleiding van koper-nikkel legeringsfilms ontwikkeld was. In overeenstemming met dit model bleek, dat Au-Pt legeringsfilms op zodanige wijze tot evenwicht komen, dat een goudrijke, stabiele samenstelling de oppervlaktefase vormt, die aan het vacuüm grenst.

Deze goudrijke legeringsfase heeft éénzelfde samenstelling voor alle legeringen met brutosamenstellingen binnen het ontmenggebied van dit systeem bij de equilibratie temperatuur. Voor dit systeem werd bewezen, dat het oppervlak van de goudrijke oppervlaktefase verrijkt wordt met platina bij langdurig contact met CO. Dit verschijnsel is met "de-alloying" aangeduid in hoofstuk VII. Dit proces is waarneembaar binnen een tijdsduur van enkele dagen bij kamertemperatuur en bij een druk van 10^{-4} Torr. Desorptie van CO door verhitting bij 573°K en verwijdering van het gedesorbeerde gas leidt tot reconstructie van de oorspronkelijke goudrijke oppervlaktesamenstelling. Deze verschijnselen zijn thermodynamisch goed te begrijpen. Het mechanisme van de verplaatsing van metaalatomen is uitgelegd door aan te nemen,dat CO corrosief gechemisorbeerd wordt door de legering waarbij vacatures in en vlakbij het grensvlak van de film worden gemaakt. Tengevolge hiervan kunnen Pt-atomen gemakkelijk vanuit de vaste bulkfase naar het oppervlak diffunderen.

De uittreearbeid van schone Au-Pt legeringsfilms is lager dan Φ_{Au} en Φ_{Pt}. Een discussie over dit nog onbegrepen verschijnsel is in hoofdstuk IX opgenomen.

In hoofdstuk VII worden resultaten met betrekking tot het zilver-palladium systeem gepresenteerd. De keuze viel op dit systeem om de oppervlaktesamenstelling te bepalen van legeringen, die een ononderbroken reeks van vaste oplossingen vormen bij de equilibratietemperatuur en om deze te toetsen aan de beginselen van het verschijnsel "de-alloying".

Aangetoond werd, dat de oppervlaktesamenstelling van deze legeringen betrekkelijk rijk aan zilver is en verandert als functie van de bruto samenstelling. De zilververrijking van het oppervlak van de schone legeringen is te begrijpen op grond van het verschil in oppervlakteenergie tussen zilver en palladium. De uittreearbeid van deze legeringen heeft een absolute waarde tussen die van de zuivere metalen.

Na langdurig contact met CO bij 293° en 373°K wordt het oppervlak van de Pd-rijke legeringen duidelijk waarneembaar verrijkt met palladium, hetgeen op grond van het verschil in adsorptiewarmte van CO op zilver en palladium verwacht werd.

De spectrale verdelingscurve van de foto-opbrengst van de met CO bedekte palladiumfilms is afwijkend van die van alle andere metalen uit de 8^e groep.

De resultaten met betrekking tot de oppervlaktesamenstelling van platina-ruthenium legeringsfilms, zijn weergegeven in hoofdstuk VIII. Het doel van dit onderzoek was de oppervlaktesamenstelling te bepalen als functie van de brutosamenstelling, als een eerste stap om het katalytisch synergisme met betrekking tot hydrogeneringsreacties van deze legeringen, waarover herhaaldelijk gepubliceerd wordt, te begrijpen. Gevonden werd, dat Pt-Ru legeringen, die bij 875°K tot evenwicht gebracht waren, een oppervlaktesamenstelling hebben, die bij benadering gelijk is aan die van het inwendige. De uittreearbeid van de schone legeringsfilms ligt tussen die van platina en ruthenium. Ruthenium is tot 50 at% mengbaar met het vlakgecentreerde kubische rooster van platina. Platina wordt tot 30 at% opgenomen in het hexagonaal dichtstgestapelde rooster van ruthenium opgenomen. Tussen 30 en 50 at% Pt zijn twee fasen aanwezig, blijkens de röntgendiffractie analyses.
Langdurig contact met CO bij 373° en 473°K resulteert niet in een merkbare verandering van de oppervlaktesamenstelling binnen een tijdsduur van dagen. Dit is in overeenstemming met bovenstaand model, daar de adsorptiewarmte van CO op platina en ruthenium ongeveer even hoog is.
In hoofdstuk IX wordt een algemene discussie gegeven over de belangrijkste aspecten van dit werk en over mogelijke gevolgen voor de kennis van het oppervlak.

Gedurende mijn onderzoek heb ik medewerking gehad van instanties en personen, die ik hier graag zou willen bedanken.
De Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Z.W.O) en de Stichting Scheikundig Onderzoek Nederland (S.O.N.) ben ik erkentelijk voor de financiële steun, die mij in staat heeft gesteld gedurende de eerste twee jaren (september 1965 - december 1967) de fundamenten van dit onderzoek te leggen.
De heer F.C.Kauffeld heeft zich met vernuft verdiept in de problematiek van de constructie van gecompliceerde fotocellen. De heer B.J.Erades dank ik voor de vlotte samenwerking bij het tot stand komen van de vele variaties in de ultrahoogvacuüm apparatuur. Het metalen instrumentarium werd vervaardigd in de instrumentmakerij o.l.v. de heer G.J.Selier.
De heer G.J.M.Lippits (chem.kand.) en drs. H.P. van Keulen hebben mij op voortreffelijke wijze geassisteerd bij een deel van het experimentele

werk. Dr.G.C. Verschoor dank ik voor zijn röntgendiffractie analyses. Het Interuniversitair Reactor Instituut o.l.v. Prof.Dr. P.J. Houtman en met name Ir. M.de Bruin en Ir. P.J.M. Korthoven ben ik dank verschuldigd voor de door hen verrichte neutronenactiveringsanalyses van de goud-platina en platina-ruthenium legeringsfilms.
Mevrouw I.E. Muller-Hordijk heeft met zorg en toewijding de offset manuscripten getypt. Mevrouw R. van Ingen-Postuma dank ik voor de correctie van een aantal manuscripten op de engelse taal.
Dr. V. Ponec en drs. B.E. Nieuwenhuys dank ik voor de verhelderende discussies die ik met hen gevoerd heb.

CURRICULUM VITAE

Na het afleggen van het eindexamen HBS-b aan het Maerlant Lyceum te 's-Gravenhage in 1958, begon ik met mijn studie in de scheikunde aan de Rijksuniversiteit te Leiden. Het candidaatsexamen, letter F, werd afgelegd in april 1962. De doctoraalstudie werd voortgezet onder leiding van de hoogleraren A.J. Staverman en M. Mandel (fysische chemie), C.J.F. Böttcher (fysisch-chemische scheidingsmethoden) en W.M.H. Sachtler (heterogene katalyse). Naast deze studie heb ik gedurende acht maanden in Z.W.O.-verband research verricht in het Gaubius Instituut. Het doctoraalexamen met als hoofdvak fysische chemie werd in juni 1965 cum laude afgelegd. Van september 1959 tot maart 1964 vervulde ik een assistentschap op de afdeling fysische chemie bij het precandidaten practicum. Van september 1965 tot en met december 1967 was ik als doctoraal assistent, vanaf januari 1968 als wetenschappelijk medewerker en vanaf september 1969 als wetenschappelijk medewerker I op de afdeling heterogene katalyse werkzaam, alwaar ik vanaf augustus 1967 de taak van conservator vervul.

STELLINGEN

I

Referentie gegevens over in ultrahoogvacuüm opgedampte metaalfilms, bijv. de electronen uittreearbeid en adsorptiewarmte, zijn slechts dan zinvol indien ze betrekking hebben op films waarvan het oppervlak volledig gestabiliseerd is.

Dit proefschrift.

II

De door Malov en Lazarev vermeende evenredigheid tussen de waarde van de electronen uittreearbeid en de sublimatiewarmte van metalen is theoretisch ongegrond en wordt door het experiment gelogenstraft.

Yu.I. Malov en V.B. Lazarev, Fiz. metal. metalloved. 26, 940 (1968).

III

Ten onrechte gebruiken Hardy an Linnett de "electron-probe micro-analysis" techniek om de oppervlaktesamenstelling van legeringen te meten.

W.A. Hardy en J.W. Linnett, Trans. Faraday Soc. 66, 447 (1970).

IV

Kotani en Akamatu maken bij de bepaling van de electronen uittreearbeid van violanthreen een aanvechtbare keuze tussen de hen ter beschikking staande referentie electroden.

M. Kotani en H. Akamatu, Bull. Chem. Soc. Jap. 43, 30 (1970).

V

De bewering van Moss en Thomas dat het oppervlak van zilver-palladium legeringen door direct contact met zuurstof verrijkt wordt met zilver is aanvechtbaar.

R.L. Moss en D.H. Thomas, J. Catalysis 8, 151 (1967).

VI

De conclusie van Jorgensen en Windridge dat 10% van het in hun heptapeptiden aanwezige histidine in de D-vorm voorkomt, is aanvechtbaar.

E.C. Jorgensen en G.C. Windridge, J. Med. Chem. 13, 352 (1970).
B. Riniker en R. Schwyzer, Helv. 44, 658 (1961).

VII

Coll en Gilding hebben niet de juiste systemen gekozen om hun theorie over de universele calibratie van de Gel Permeatie Chromatograaf experimenteel te verifiëren.

H. Coll en D.K. Gilding, J. Polym. Sci. A. 8, 89 (1970).

VIII

De door Takashima afgeleide uitdrukking voor de polariseerbaarheid van een poly-ion in aanwezigheid van tegenionen is onjuist als gevolg van een principieel verkeerde statistisch-mechanische middelingsprocedure.

S. Takashima, Biopolymers 5, 899 (1967).

IX

Bij de bestrijding van de luchtverontreiniging als gevolg van de toenemende industrialisering en bepaalde aspecten van de persoonlijke welvaart zal de heterogene katalyse een steeds belangrijker rol gaan spelen.

X

Een wikkeleurige greep uit het maandblad "de Consumentengids" levert met grote waarschijnlijkheid stellingwaardig materiaal op.

De Consumentengids, willekeurige greep.

R. Bouwman

Leiden, 4 november 1970