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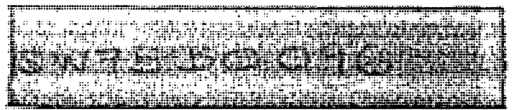

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SURFACE ANALYSIS IN METALS BY MEANS OF CHARGED PARTICLE INDUCED REACTIONS

by

JOACHIM LORENZEN

UPPSALA 1975

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Doctoral dissertation
by
Joachim Lorenzen
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JOACHIM LORENZEN

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Doctoral thesis at Uppsala University 1975
ISBN 91-554-0263-1

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Printed in Sweden by
AB Atomenergis Kontorstryckeri, Nyköping 1975

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I INTRODUCTION

In recent years there has been an increasing demand for analytical methods to measure the concentration and the depth distribution of various elements in different matrices. In metallurgy rapid, low-cost, multi-element detection methods are required, that are capable of reliably mapping the distribution of light elements in the metal surface. Dynamical processes, such as corrosion and the transport of oxygen under specified thermal conditions, are of interest in a variety of contexts as, for example, in the design of reactor fuel cladding material.

A range of techniques, that have been recently devised, and which facilitate the analysis of a special group of elements in a well defined surface layer of a given matrix, have one thing in common, namely that they are based on the principle of charged particle induced reactions. Owing to their limited penetration into matter charged particles provide an ideal tool for surface analysis.

This thesis comprises some experimental investigations which extend the flora of analytical techniques for the quantitative measurement of low concentrations and their depth determination in metal surfaces by means of charged particle induced reactions. To date there is no method which is so general that it could be successfully applied to all types of samples. The development of new quantitative techniques that are capable of assaying specified elements under real conditions might therefore make a valuable contribution to analytical work.

In order to understand the relation between the experimental techniques that form the basis of this thesis and the analytical methods that are at present available this work includes a survey of the literature on this subject. The papers presented here are then summerized at relevant places in this review of the state of the art of measuring low concentrations and determining concentration profiles of both light and heavy nuclides in a wide range of matrices.

Preliminary results concerning parts of this work have been presented at the following meetings:

1 Nordic Conference on Trace Elements
Aarhus, Danmark, 1971

2 Conference in Physics
Lund, Sweden, 1972

3 International Meeting on Activation Analysis
Saclay, France, 1972

The thesis includes the following papers:

I Ahlberg M. Akselsson R, Brune D and Lorenzen J
Proton-induced X-ray analysis of steel surfaces for microprobe purposes.
Nucl Instr Meth 123 (1975) 385.

II Lorenzen J and Brune D
Determination of oxygen in zircaloy surfaces by means of charged particle activation analysis.
Nucl Instr Meth 123 (1975) 379.

III Lorenzen J
Depth distribution studies of carbon in steel surfaces by means of the nuclear reaction $^{12}C(p,\gamma)^{13}N$.
Nucl Instr Meth 121 (1974) 467.

IV Lorenzen J
Depth distribution studies of carbon, oxygen and nitrogen in metal surfaces by means of neutron spectrometry.
AE-502 (1975).

II CONCENTRATION MEASUREMENTS

1 General remarks

The elemental composition of solids can be studied by means of charged particle induced reactions. For such investigations "Surface analysis" is a fundamental term. The reader may probably understand what is meant by the surface of a solid, although there is no quantitative, physical definition found in the literature. In fact, the term "surface" is confusingly used with different interpretations. Sometimes it may define a boundary, a starting point for in-depth calculations; sometimes it refers to the front zone of the specimen which is to be explored. The author whishes to make clear, that in the following discussion surface is to be understood as the upmost layer of material in the sample. The thickness of this layer, however, is defined by the range of the charged particles used in the analytical method concerned. This definition allows a distinct difference to be made between surface analysis, which controls the first atomic layers of the specimen, and bulk analysis, which extends over the whole volume of the sample.

The study of the physical and chemical phenomena that take place in the surface of solids requires the quantitative determination and location in depth of elements in very small amounts. In this context charged particle induced reactions offer the possibility of non-destructive investigations with a high degree of sensitivity and selectivity.

Neutron and photon activation analysis can be used with advantage to measure bulk impurities of elements in trace quantities in thick samples. Owing, however, to the limited range of ions in matter charged particle induced reactions are specificly useful for concentration measurements in the surface of substrates. They allow studies in fundamental problems related to metallurgy such as diffusion phenomena, growth mechanisms on thin films, corrosion phenomena, trace contamination of surfaces, ion implantation etc.

Generally, the quantitative methods can be divided into two groups: the first contains methods which permit measurement of the concentration of the elements concerned, the second contains methods, that also include the determination of the concentration profile as a function of depth.

The methods considered here are consequently discussed in two separate chapters, depending on whether they belong to the first group or the second.

Some definitions

The capability of the various techniques can be indicated by the use of different parameters. Concentrations are usually given in per cent. For very small amounts, however, the sensitivity can be expressed in ppm (parts per million) or ppb (parts per billion), which denotes the ratio of the trace quantities detected to the number of matrix atoms in the analysed volume. Detection limits can be given in µg and ng, or as the minimum number of atoms to be detected (e.g. 10^{-15} atoms/cm^3). Values expressed in µg/cm^2 actually concern a layer of material. Resolution might also be expressed in atomic layers. A monolayer is defined by $N^{2/3}$ where N is the number of host atoms per cm^3. Alternatively resolution can be given in µm (10^{-6}m) or ångström units (1Å = 10^{-10}m).

The term "effective range" or "effective depth" is sometimes used for the total surface region in which the concentration is measured. This parameter has been developed out of the necessity to distinguish between the range of the charged particle and that part of the range within which nuclear reactions are energetically possible. For nuclear reactions with negative Q-values no radiation can be emitted for particle energies below threshold, i.e. beyond the "effective range".

The quantitative measurement of X-rays provides information about the elemental concentration in the sample surface. Due to the energy dependence of the production cross-section and of the attenuation of the emerging X-rays the contribution of a given atom to the total radiation emitted, depends on its location within the surface. Many authors have therefore adopted the term "effective depth" to denote the volume within which a certain part of the total radiation is produced.

2 Microanalysis by means of non-nuclear reactions

The most important non-nuclear methods for quantitative surface analysis are Rutherford scattering, ion-induced X-ray-emission and Auger electron spectroscopy. They have been applied to surface analysis in metals and [illegible] a comprehensive description dealing with the complementary nature of these and other techniques has been given by Mayer and Turos [1]. The

capability of these methods is indicated and a variety of examples for their application has been collected in the very carefully written review article of Lukas [2].

Electron spectroscopy will not be further discussed here since this has already been dealt with in a rigorous manner by Siegbahn et al. [3] in their well known ESCA-book.

Rutherford scattering an ion-induced X-ray emission

Elastic scattering and X-ray production have some interesting features in common. The analytical principle of Rutherford scattering is based on the knowledge of the kinetics of atomic encounters. A mono-energetic beam striking the surface atoms of a target matrix, is scattered in such a way that the energy of the emitted particles, observed within a given angle, increases with the mass of the scattering atom. The energies of the characteristic X-rays produced in the atomic collision with the incident ions are also an increasing function of the atomic number of the matrix element (Moseley's law). Accordingly the measurement of the energy spectrum of Rutherford scattered charged particles and of the emitted characteristic X-rays provides fundamental information about the atomic species that are simultaneously present in the matrix. This corresponds to a quantitative multi-element analysis.

The impinging charged particle loses energy when penetrating the matrix and so does the scattered ion. With regard to backscattering the thickness of the analysable layer is thus much smaller than the range of the bombarding particle. Owing to the increased absorption of soft X-rays only a negligible part of the yield produced at greater depths can reach the detector. Both methods are thus typically suited to surface analysis.

A third factor, the supreme elemental resolution, i.e. the separation of adjacent atomic numbers, which is a feature of both Rutherford scattering and ion-induced X-ray emission, makes both methods highly attractive for multi-element surface analysis. Owing, however, to the stopping power of the matrix a particle scattered at a given depth is emitted with an energy lower than that of a surface-scattered ion. This fact results in an ambiguity; a surface emitted particle scattered by an atom of a given mass may have the same energy as a particle scattered by an atom of larger mass positioned at greater depth. The consequence of this is that heavy atoms in light matrices may be detected without interference whereas, in thick targets

at least, light elements in heavy matrices are hardly analysable [4]. The same is true for analysis by means of X-ray measurements as a result of the increase of self-absorption for the lower X-ray energies emitted from lighter elements in a matrix consisting of heavy atoms.

As far as Rutherford scattering is concerned this inadequacy is compensated for by the application of forward scattering and "channeling".

Special applications in Rutherford scattering

Forward scattering has been successfully applied to the determination of carbon in silicon [5]. The sample used had a thickness of 9 000 Å and was contaminated with carbon on both the front and the back surface. Energy spectra for 1.8 MeV and 1.0 MeV He^{+}-ions were measured at 90° relative to the incident beam direction for forward and backscattered ions. The forward scattered ions from the two carbon layers were distinctly resolved and also separated from the broader matrix contribution. This method is supposed to provide a sensitivity of a few monolayers.

Ions which are allowed to strike a crystal surface at a well-defined, so called, critical angle can penetrate deep into the crystalline material. They are then gently steered through the "channels" in the atomic lattice by correlated collisions. Well-channeled ions do not come closer to the lattice rows than, approximately, the Thomas-Fermi screening distance which is of the order of 0.1 Å. Consequently no atomic or nuclear encounter can take place unless the atoms are displaced from their lattice sites by more than this value. Accordingly, on irradiating a crystal and applying the channeling technique the contribution made by the matrix atoms to the emitted radiation arises mainly from the first atomic layers. Impurities that are located at interstitial positions are exposed, however, to the ion beam even at greater depths. From this it can be understood that the signal-to-background ratio is considerably increased, by the order of two magnitudes, compared with measurements made in a "random direction" or on amorphous targets.

The channeling technique is frequently applied to the measurement of the disorder in crystals created by radiation damage [6], or to phase structure studies in polycrystalline material [7]. In this context the different sublattices of one crystal are often measured separately by applying a nuclear technique to the detection of the light element and a non-nuclear method for studying the heavy sublattice.

Low energy backscattering has also become an attractive technique in analytical work. Systematic studies have shown that a maximum in the scattering cross-section is reached at energies of about 3 keV. At these energies background is reduced due to the absence of nuclear reactions. The general features of this technique have been described in a review article by Smith [8].

Proton-induced X-ray emission

Proton-induced X-ray emission (PIXE) has the great advantage of a low Bremsstrahlung contribution as compared with the X-ray emission produced by photons and electrons. This technique has been developed into a versatile tool for microanalysis by Johansson and co-workers [9]. These authers report a detection limit of about 10^{-12}g obtained by irradiating small samples (~ 1 cm^2) with protons at energies between 1.5 and 2.5 MeV and a current of about 1 μA. With this technique all elements of the periodic table with Z > 15 can be studied simultaneously if the sample can be applied to thin supporting high purity carbon foils (~ 40 $\mu g/cm^2$).

The background- Bremsstrahlung observed in PIXE spectra is due to the production of secondary electrons which have received kinetic energy by collision throughout the range of the primary particles. The use of thin backing foils is therefore necessary if background radiation is to be reduced appreciably. Furthermore, thin target foils render corrections for self-absorption unnecessary.

It is well known that the ionization cross-section increases with the energy of the protons up to a certain maximum value. The energy dependence of these maxima, however, is a decreasing function of the atomic number of the target atom. For Ca, Ti and Ni for instance the value of $\sigma(p, X_K)$ attains a maximum of 5 000 b, 4 000 b and 1 500 b at energies of 8.5 MeV, 10.4 MeV and 16.6 MeV, respectively [10]. The cross-section also increases with the mass and the multiplicity of the X-ray generating ion (~ Z^2). However, the maximum energy E_e of secondary electrons (m_e), which give rise to Bremsstrahlung, can be calculated from the mass (M) and the kinetic energy (E_{ion}) of the ion by using the expression

$$E_e = \frac{4Mm_e}{(M + m_e)^2} E_{ion}$$

A direct consequence of this relationship is that the Bremsstrahlung energy increases with the energy of the accelerated ion. Thus, the increase of sensitivity due to larger cross-section values is counteracted by enhanced background under the photo peak (e.g. E_e = 20 keV for 10 MeV protons, which corresponds to a Bremsstrahlung continuum up to Z = 45 (Rh)).

It is also necessary to take the effects of Compton scattering and of nuclear reactions into consideration. The problem arising from the induced background in high energy, charged-particle induced X-ray emission has been treated in detail by Folkmann and co-workers [11]. Their study indicates that the sensitivities attainable by this technique extend to values of 1 to 0.1 ppm.

The question therefore arises whether the detection limits observed could be further decreased by an optimal choice of ions and their kinetic energy. This problem has been investigated to a certain extent by Herman and co-workers [12]. Their experimental studies with protons (2-10 MeV), alpha particles (6-25 MeV) and $^{16}O^+$-ions (6-40 MeV) indicate strongly that 2.2 MeV protons and 6 MeV alpha particles are the most suitable energies and ions for use in analytical work. Despite the favourable increase in cross-section with ion energy ($d\sigma/dE_{ion}$ ~ 120 barn/MeV) the enhanced background due to Bremsstrahlung and nuclear reactions makes a significant reduction in the signal-to-noise ratio. Owing to their shorter range, heavier ions deposit more energy in the thin backing foils than do protons so that the supporting backing can be destroyed due to increased heating. Lower currents must therefore be used in such instances.

Sensitivity studies have been extended to the use of protons, α-particles and ^{16}O-ions at energies of 1-5 MeV/amu [13]. On the basis of a careful analysis of the different background contributions it was found that of these three ions protons at energies between 1 and 4 MeV are the best suited to analytical work.

The investigations of Watson and co-workers [14] about the analytical capabilities of X-ray emission induced by 50 MeV α-particles indicate that sensitivities of 50 ppm could be obtained for elements with Z between 22 and 50 and of 130 ppm for elements with Z > 50. In particular they reported that the detection limits for Cu, Sn and Pb deposited on 1 $\mu g/cm^2$ VYNS backings were 1.9 10^{-12} g, 3.2 10^{-12} g and 5.5 10^{-12} g, respectively.

Sensitivities at even higher α-energies (up to 80 MeV) have been investigated as a function of the atomic number of the target, backing thickness,

beam charge, energy and flux of the incident charged particles [15]. The conclusions of these measurements are in agreement with those of the earlier mentioned, namely that no improvement of sensitivity is obtained on using ions with increased energies.

PIXE applied to thick targets

The tendency towards the use of thick targets in connection with PIXE demands improved knowledge of cross-section values. Measurements of ionization cross-sections have been carried out for Fe, Co, Cu, Zn, Ga, Ge and As using protons at energies between 0.5 MeV and 2.0 MeV. This compilation is useful for the application of PIXE to the study of thick targets [16]. Cross-sections for C, Mg, Al, Cu, Nd, Sm, Gd, Tb, Dy and Ho at proton energies between 15 and 1 900 keV in thick targets have been compiled by Khan and co-workers [17,18]; who were also the first to use PIXE for analytical work.

A comparison between the cross-section values obtained by (α, X)- and (Ne^{2+}, X)-reactions measured in thin and thick metal targets (Al, Cu, Ag and Au) in the energy region 1 to 5 MeV has been recently reported [19]. For K and L X-rays the agreement was excellent, whereas for M X-rays the approach was unsatisfactory owing to large uncertainties in the self-absorption corrections.

The Sn $K_α/K_β$-ratio has been studied as a function of the sample thickness [20]. The experimentally obtained results were compared with theoretically predicted values and a 20 % discrepancy was found and subsequently accounted for in terms of a thickness effect. This experiment emphasizes that special care must be taken when PIXE is applied to thick targets.

It is intended that PIXE should be applied to proton microbeam studies, which are under development in the VdG laboratory at Studsvik [21]. Measurement of the detection limits that are valid for thick targets was therefore of special interest. This investigation is described in Paper I. Microbeam conditions were simulated by a narrow beam 2 mm in diameter and by a proton current of the order of 10-100 nA. When thick targets are used the main contribution to the X-ray yield is consequently made by the matrix atoms to nearly 100 %. The dominating yield due to the matrix can be suppressed, however, by introducing an absorber (X-ray filter) with an absorption edge corresponding to the energy of the characteristic X-ray line emitted from the matrix. Accordingly, in the experiments involving steel targets the Fe $K_α$-(6.403 keV) and Fe $K_β$-(7.057 keV) lines are strongly attenuated by the absorption edge of chromium (5.99 keV). A chromium absorber, 12.5 μm thick, was therefore used in these experiments and the transmission of the Fe $K_α$-radiation was consequently reduced to 1.5 %. Owing to the absorption function of Cr, the transmission of X-rays for elements with Z > 26 (iron) is increased to more than 10 % above 10 keV.

Since attenuation is a continously increasing function of the absorber thickness Mylar foils of two different thicknesses (920 μm and 4 000 μm) were also used. From these experiments it was found that the thicker Mylar foil can successfully be applied when X-rays with energies above 7 keV are to be studied (Elements with Z > 28). The detection limits obtained by this technique are of the order 10-100 ppm for a running time of 1 000 sec.

Owing to the variation of the effective proton range with energy and to the increase of X-ray attenuation with depth of production only a part of the X-ray yield emitted from a certain element at a given depth below the surface can reach the detector. The parameter "effective depth" has been introduced to describe what fraction of the X-ray yield produced within a given layer contributes to the measured spectrum. This concept can thus be used to facilitate quantitative depth profile analysis. This topic will be discussed in a later section. However, in this connection the "semi-quantitative depth distribution study" of chromium in an iron surface is worth mentioning [22]. In that study comparison was made between the Cr $K_α$/Fe $K_α$ ratios obtained by irradiation with 150 keV and 400 keV protons, respectively. Information was thus gathered about the change of the Cr-concentration in a 0.25 μm surface layer compared to that of the first 1 μm. About 90 % of the Cr $K_α$ yield was measured in each instance.

Another elegant application of the idea of "effective depth" is illustrated by the work of Needham and co-workers [23]. They were able to measure oxide films with thicknesses ranging between 10 and 200 Å using 120 keV protons. Because of the limited range of these low energy protons and the 1/e-attenuation for oxygen X-rays ($K_α$ = 523 keV) in a surface layer of 1 485 Å there is a negligible contribution from the low oxygen bulk concentration in the matrix (2.3 ppm Fe_3O_4) by comparison with the yield emitted from the first few monolayers in the surface. On the basis of this

principle the growth rate of oxygen in the surface of Battelle-iron was determined for temperatures between 200 and 350°C.

In recent studies Musket [24] clearly demonstrated the feasibility of PIXE at low X-ray energies by the quantitative detection of the light elements including boron. In this experiment polished boron, polished graphite, copper and anodized aluminum targets were irradiated with 350 keV protons and the characteristic X-rays B K_α, C K_α, O K_α, Cu $L_{\alpha,\beta}$ and Al $K_{\alpha,\beta}$ were observed using a windowless Si(Li) detector.

The results mentioned in this chapter show that non-nuclear techniques allow quantitative measurement of low concentrations throughout almost the entire periodic system. However, whereas these techniques can be used to determine heavy nuclei, nuclear methods which are described in the following chapter appear to be useful for the quantitative assay of light elements.

3 Microanalysis by means of nuclear reactions

Nuclear techniques provide an alternative means for determining small amounts of nuclei. For analytical work protons, deuterons, tritons, ^{3}He, ^{4}He and α-particles have been used since long in the energy region 0.5 to 5 MeV per nucleon. Recently heavier ions such as ^{12}C, ^{16}O and the ions of the noble gases have been applied to the investigation of thin surface layers. Beam currents are chosen in the range of nA to several μA depending on the type of target. Low currents may be necessary in order to avoid thermal destruction and radiation damage or in order to reduce the dead-time.

Nuclear reactions induced by charged particles are hindered by the Coulomb field of the target atom. The Coulomb barrier which is proportional to the atomic number Z of the bombarded atom is thus lower for lighter elements. This is important for analytical purposes. Consequently this technique is best suited to the detection of light impurities in a heavy matrix.

Microanalysis by charged particle induced nuclear reactions was first applied in 1962 by Amsel [25], in studies of the oxygen transport in anodic aluminum oxide. He recently published a very extensive compilation covering the nuclear microanalysis of light elements [26] and reported that ^{2}H, ^{6}Li, ^{7}Li, ^{12}C, ^{14}N, ^{16}O, ^{18}O, ^{19}F and ^{27}Al are routinely determined in a 2 MeV-VdG laboratory. Albert described the microanalysis of oxygen, carbon and nitrogen by means of proton, deuteron and triton irradiation

[27]. Applying nuclear reactions detection limits between 10^{-2} μg and 10^{-4} μg (corresponding to 10^{-4} - 10^{-6} ppm) can be achieved for light elements in metals. It should be stressed that these values could be obtained only in targets that feature high purity. The result might be compared with the detection limits for activation analysis by γ-photons (10^{-2} μg) [28] and by neutrons (10^{-3} μg, for medium and heavy nuclei) [29]. For low concentration bulk measurements, however, using thermal, epithermal or fast neutrons, as well as photons generally chemical separation must be applied in order to achieve extreme sensitivities.

It is well known that the use of tritons and ^{3}He-particles, especially at higher energies, provides extremely low detection limits. Because of their low binding energy (8.482 MeV and 7.717 MeV, respectively) they can undergo many nuclear reactions that are exoergic. The systematic compilation of Markowitz and Mahony [30] on the use of ^{3}He-induced activation analysis has become classical. The list of elements that can be studied successfully in these reactions ranges from ^{6}Li to ^{48}Ca.

Tritons are not so frequently used in view of the accompanying risk for contamination of the facility due to this active ion. For the quantitative analysis of oxygen 2 MeV triton-irradiations of "very pure van Arkel zirconium" have been reported [31]. Measurement was made of the 511 keV-decay activity of ^{18}F ($T_{1/2}$ = 109.7 min) and a detection limit of 5 10^{-3} μg/cm^{2} oxygen was claimed.

Fast methods

In many applications the material to be studied is rarely of extreme purity. On the other hand, easily managed analytical methods are required with good sensitivity and a high degree of rapidity. In this connection a fast, non-destructive technique for measuring low concentrations of oxygen in zircaloy has been developed. This experiment is described in Paper II. In this work zirconium oxide and zircaloy samples (800 ppm oxygen) were irradiated with deuterons at energies of 2.3, 2.6 and 3.0 MeV. The method employs the comparison of the yield of promptly emitted 870 keV γ-rays produced in the reaction ^{16}O(d,pγ)^{17}O with the activity from the reaction ^{16}O(d,n)^{17}F. ^{17}F is a β^{+}-emitter ($\tau_{1/2}$ = 67 sec) which produces 511 keV-annihilation radiation. It was found that, while for the activity measurement, the detection limit is dependent on the initial deuteron energy (40 ppm at 3.0 MeV) the prompt γ-ray measurement provided a

constant detection limit of 10 ppm ($7\ 10^{-2}\ \mu g/cm^2$). The result is discussed in the light of the "effective range" of the deuterons and the difference in cross-section of both reactions. These measurements demonstrated that a total amount of $2\ 10^{-8}$ g oxygen can be detected within the effective depth of 20-30 µm in the zircaloy samples. The running time for an irradiation yielding 1 % statistical uncertainty for each sample was about 60 sec, which clearly demonstrates the rapidity of the technique.

Another fast method for the determination of nitrogen in single seeds has been reported recently [32]. The light elements present in the surface of single grains were studied by deuteron induced reactions. Nitrogen concentrations of 1.5 to 3.5 % have been determined measuring the energy spectra of the emitted protons and α-particles. Running times of the order of 20 sec were sufficient to achieve a statistical uncertainty of 5 %. The authors expect it to be possible to decrease the time of irradiation in the near future to 1 sec for routine analysis. It has been observed during the course of these experiments that up to a few per cent of the total volume of the grain might be destroyed by the beam. The result of this effect should be studied separately.

Some experimental problems in connection with the determination of light elements in metallic targets using charged particle induced reactions have been described by Weber and Quaglia [33]. Phenomena concerning the target behaviour such as oxygen content decay, wear effects and carbon build-up are instructively discussed and can be avoided if corresponding precautions are taken by the experimentalist.

A special technique for the reduction of background and interferences has been developed by Pretorius [34]. This technique is based on the coincident measurement of complementary particles (CMCP). The energy of the complementary particles emitted in the nuclear reactions of charged particles with light elements are measured by separate detectors. The correlation between the energies of such particles and the given angles at which they are simultaneously emitted is given by classical nuclear kinetics. This method has been applied to the measurement of ^6Li and ^7Li in natural samples [35]. Thin targets of 10 to 200 $\mu g/cm^2$ thickness were irradiated using 1.9 MeV protons and deuterons and the emerging α-particles and $^3He/^4He$-particles were measured in forward and backward directions. The irradiations lasted for 3 to 10 min. A comparison between spectra with and without coincidence clearly demonstrates the ability of this method to suppress any kind of interference.

The methods described in this chapter are capable of detecting small amounts of impurity in the surface of various matrices. However, the concentrations measured in this way might not be representative for the bulk composition of the sample. Such an assumption can be disastrous for inhomogeneous distributions. It should be emphasized that the concept of the "effective range" offers the possibility of relating the measured concentration value to a limited volume in the specimen. In the following chapter methods will be discussed that can be used to measure inhomogeneous concentration distributions.

II DEPTH DISTRIBUTION STUDIES

4 General remarks

The aim of depth distribution studies is to gather information about the amount of a given element present in a well defined layer in the surface of a solid. The thickness of this layer can be chosen arbitrarily but the lowest value that can be obtained is determined by the resolution of each technique. The minimum layers attainable by the different methods that have been developed range from parts of monolayers, measured in several Ångström units, to "slices", some micrometers thick. The depth over which the concentrations are measured are logically in direct correspondence to the resolution and vice versa.

In general each method belongs to one of the following principle groups.

5 Sectioning technique

This technique is based on the preparation of consecutive "slices" of the specimen, taken in a direction perpendicular to the beam axis, in such a way that the concentration of the element to be studied is not affected. The amount of the element present in each slice is then measured separately. The analyses belonging to this group are definitely destructive.

The technique is applicable to any quantitative method available. On a point of curiosity it is worth mentioning that neutron activation analysis, which is typically adopted for bulk measurements, has been used in this way to study the concentration profiles of phosphor and gallium in silicon [36]. In this instance layer sectioning was performed by means of wet etching at a rate of 2 µm/min and the neutron induced activity in each

layer was subsequently measured by means of γ-spectrometry.

Concentration profiles of tritium in zircaloy-2 have been studied by the successive removal of sections ranging from 1 to 2 μm in thickness using chemical polishing [37]. The $^{6}Li(n, \alpha)^{3}H$-reaction was used to inject tritium into the specimens. The diffusion profile was subsequently measured by monitoring the amount of tritium in each layer using radioassay techniques and with the help of a gas flow proportional counter.

The nature of "sectioning" varies with the application. Common techniques are pure chemical dissolution, electrochemical anodization and subsequent selective dissolution of the oxide, vibratory mechanical polishing and sputtering. Mechanical grinding is often used in connection with microscopical studies.

Fine-stepping profile measurements benefit from the erosion properties of bombarding ions when using an ion microprobe. The rate at which the target material is sputtered away depends on the yield of the accelerated ion and the ratio of the atomic masses in the collision. Concentration profiles of boron implanted in silicon have been measured with 5-50 keV argon ions at a sputtering rate of the order of 200-400 Å/min and at a depth resolution ~ 200 Å [38]. The quantitative analysis of profiles based on this technique assumes that the sputtering rate is constant. However, deviations from linearity have been observed in the first resolvable layers [39]. The sputtering technique has further been utilized for profile measurements of oxide films in various metals [40, 41]. A comprehensive review article dealing with the analytical applications of the ion microprobe is given by Bayard [42].

The measurement of a concentration profile using the sectioning technique can be a rather long and tedious operation. Consequently, automatization of this process in an invaluable asset.

An automated system for the analysis of impurity concentration profiles in silicon has recently been reported [43]. The method is based on neutron activation of the specimen for a period of 2-15 days. This is followed by sequential sectioning performed by anodic oxidation and stripping in steps of 150-700 Å. The total analysis takes about 1 hour. Since most of the activated nuclides are strong β-emitters Čerenkov-radiation counting is used for the element assay. Concentrations as low as 10^{7} atoms/cm^{3} have been determined.

6 Scanning techniques

A second direct method, the scanning technique, employs focussed beams. A beam with a diameter of the order of micrometers is made to traverse a polished sagittal cut of the target material. Measurement of the emitted radiation from a chosen element as a function of the translatation provides information about the concentration distribution of that element with depth. Movement in lateral direction is provided by the beam, using electrostatic deflection or of the sample, employing x-y-tables. The analyses accomplished with these techniques can be non-destructive.

This technique is usually applied in electron microprobe studies [44]. By traversing the electron beam over the target area in a certain pattern (raster) it is possible to determine the spatial concentration distribution of nearly all elements of the periodic table.

Pierce applied this technique in microbeam studies as early as 1967 [45]. He reported the use of well collimated proton beams (30-180 μm) for elemental and surface layer analysis. Protons with energies between 0.5 and 5 MeV were directed at samples attached to a support, that could be moved perpendicular to the beam direction using micrometer screws. Lateral concentration distributions were measured by backscattering and γ-emission produced by nuclear reactions.

A further development of the proton microbeam technique has made possible the production of a 4 μm-diameter 3 MeV proton beam [46]. This raises the lateral resolution to a level comparable to that obtained with electron microbeams.

In a recently published work by Pierce and co-workers [47] scanning microbeam technique was applied to the measurement of carbon diffusion profiles in steel. Carbon concentrations were determined by proton spectroscopy and X-ray measurement induced by 1.3 MeV deuterons. It is reported that carbon determination using the scanning technique suffers from carbon build-up on the specimen surface. A special cooling finger had to be devised in order to eliminate this disturbing effect.

In the same laboratory a method was developed for profile measurements of magnesium in aluminum [48]. For this purpose measurement of the proton spectrum due to (d, p)-reactions was applied in preference to the analysis of fast neutrons from (d, n)-reactions. The reported sensitivity for the detection of Mg in the light Al matrix was 0.37 % (by mass) at an optimum deuteron energy of 1.80 MeV.

7 Resonance reactions

The occurrence of resonances in the cross-sections of nuclear reactions is a well known phenomenon. Charged particle induced nuclear reactions that exhibit sharp resonances in the keV-MeV region provide a powerful tool for depth distribution studies.

Assume that a nuclear reaction A(p, γ)B has a resonance at $E_p = E_{res}$. When protons with an energy E_{res} strike a target that contains element A the γ-yield is mainly due to the production of nuclide B in the uppermost layers of the target. On penetrating into the target the protons lose energy (due to the stopping power (dE/dx) of the matrix) and this is followed by a reduction of the reaction cross-section since E_p is now less than E_{res}. If E_p is raised to E_p + dE the protons have to penetrate a layer of the target surface of thickness dx, defined by dE $(dE/dx)^{-1}$ before the kinetic energy is reduced to $E_p = E_{res}$. The resonant part of the cross-section is thus responsible for the γ-ray production within a layer below the surface. Progressive increase of the particle energy permits a measurement of the concentration of A at subsequent depths and the depth profile can be established. The thickness of the different layers defined in the analysis is a function of the width of the resonance, the stopping power of the matrix and the energy uncertainty at the instant of resonant reaction, the so-called straggling. The existence of sharp resonances in many charged particle induced nuclear reactions in the energy range of 100 keV to some MeV has encouraged application and study of this technique in many Van de Graaff laboratories. A list of energies for which (p, γ)-resonances occur has already been published [49].

The analytical applications of (p, γ)-resonance reactions for proton energies of 0.5 MeV have been described by Pierce [50]. In this paper resonance reactions for the light elements lithium to sulphur have been compiled. Data that are necessary for the analysis of these elements are included. It should be mentioned that not all of the reactions chosen in this work are suitable for profile measurements. The presence of multiple resonances leads to interference and complicates the analysis.

The classical example that demonstrates the usefulness of this method is the detection of fluorine in zircaloy [51]. The nuclear reaction $^{19}F(p, \alpha\gamma)^{16}O$ exhibits two suitable resonances at E_{p1} = 1 348 keV and E_{p2} = 1 375 keV with values σ_1 = 340 mb (FWHM = 11 keV) and σ_2 = = 158 mb. Measurement of the emitted γ-rays in the energy range of 6.1 to 7.1 MeV has permitted determination of fluorine concentrations down to (0.01 ± 20 % μg/cm^2) in surface layers less than 0.1 μm thick.

The fact that the cross-section function exhibits two resonances close to each other complicates the analysis since, in order to establish the concentration profile, it is necessary to solve a set of linear equations determined by the number of depth layers.

Since straggling leads to a deterioration of the spatial resolution at greater depths these workers recommend the application of sectioning-techniques in combination with the (p, αγ)-reaction for surface analysis.

In a work reported by Mackintosh [52] the same reaction is employed but the use of comparative standards removes the need for accurate knowledge of the proton flux and detector efficiency. This approach still suffers from the absence of a single resonance.

Depth profile determinations of Al in the surface of SiO_2 have been reported by Dunning [53], who made use of the nuclear reaction $^{27}Al(p, \gamma)^{28}Si$. This exhibits a sharp resonance (FWHM = 100 eV) at a proton energy of E_p = 991.9 keV. The depth resolution afforded by the reaction is of the order of 100 Å. The time required to determine the depth yield curve for a 4 μm thick layer was about 2 hours.

Recently this technique has been extended to the profile measurement of sodium [54] using the reaction $^{23}Na(p, \gamma)^{24}Mg$, which has a resonance at E_p = 1 416.8 keV (FWHM = 90 eV). Detection limits of the order of 10^{13} atoms/cm^2 are claimed for favorable host-impurity combinations provided that the impurity atoms lie in the upper 10^3 Å of the specimen. A sensitivity of about 1 ppm coupled with a spatial resolution of < 20 Å demonstrates the feasibility of (p, γ)-reactions for profiling techniques. It should be mentioned that the emission of high energy γ-rays (^{19}F: 6.1-7.1 MeV, ^{27}Al and ^{23}Na: 9.5-14 MeV) favours a high signal-to-noise ratio for the measured γ-radiation.

An attempt has been made to determine carbon concentration profiles in steel surfaces by means of the (p, γ)-resonance technique [55]. In this instance measurement was made of the prompt 2.365 MeV and 3.510 MeV γ-rays emitted from the residual ^{13}N nucleus. At these energies prompt γ-rays suffer interference from the background radiation continuum. Thus the low sensitivity obtained in these measurements is a consequence of the poor signal-to-background ratio. Carbon, however, is one of the most important components in steel and there is, quite naturally considerable

interest in the possibility of developing a sensitive carbon profiling technique.

Depth distribution studies concerning carbon in steel surfaces have therefore been continued. These studies employ the measurement of the 511 keV-annihilation radiation emitted as a result of the proton activation of carbon and are reported in Paper III. The residual nucleus ^{13}N is a β^+-emitter (E_0 = 1.19 MeV) with a half-life of 10.0 min. The efficiency of the NaI(Tl)-crystal used is by a factor of 3 greater for 511 keV γ-rays than for the prompt γ-rays around 3 MeV. The probability for the detection of one of two annihilation quanta is also greater than that for a single prompt γ-ray. By utilizing a low- background detection chamber for post-irradiation γ-ray measurement and increasing the solid angle it was finally possible to raise the sensitivity by more than an order of a magnitude. The running time was now decreased from several hours to a period comprising the irradiation time of 10 min followed by the subsequent measurement of the decay activity for two half-lives.

In real samples carbon depth distributions are of interest over the first 10 to 20 μm. Thus, straggling effects that are pronounced at greater depths are necessarily included in the analysis. The cross-section of the nuclear reaction $^{12}C(p,\gamma)^{13}N$ exhibits two resonances, at E_{p1} = 456.8 keV (σ_1 = 127 μb, FWHM = 36.5 keV) and at E_{p2} = 1 698 keV (σ_2 = 35 μb, FWHM = 72 keV). The difference of 1 241 keV between the two resonances makes possible the analysis of a carbon profile within a 13 μm thick surface region, using the first resonance only.

Steel samples with inhomogeneous carbon concentrations were prepared and measured by the developed technique. Absolute concentrations were determined by comparison with carefully homogenized standard samples at corresponding incident energies. It was thus possible to avoid making otherwise necessary corrections for the self-absorption at higher proton energies and to exclude errors due to uncertainties in the cross-section.

Reliability of the method was demonstrated by the measurement of a steel sample featuring a decarburized surface zone extending to 4 μm at levels of 0.15 to 1.2 % carbon. This gradient was determined by employing both resonances. Microscopical measurements and the application of the (d, n)-method (to be explained in Paper IV) confirmed the result.

The depth resolution, that can be obtained ranges from 0.25 μm at the surface to about 0.6 μm at a depth of 10 μm. The detection limit of 0.1 % is due to the low values of the resonant cross-section. This is offset,

however, by the fact that in steel the carbon concentrations of the gradients are of the order of per cent.

The technique of using (p, γ)-resonances for profile measurements has been applied to ^{28}Si and ^{32}S, in order to investigate their dopant distribution in the semiconductor material GaSb [56]. Both elements exhibit several resonances in the MeV-region and the measurements were therefore concentrated on depth layers below 3 μm with a depth resolution of 0.2 μm.

The emitted prompt γ-rays were detected with a Ge(Li)-detector, which enables simultaneous measurement to be made on several dopants. The sensitivities for Zn, Si and S were 300 ppm, 90 ppm and 700 ppm respectively, obtained levels, which correspond to detection limits of the order of nanograms for the dopants measured.

Resonance reactions are not restricted to the measurement of γ-rays. Concentration profiles of the light element oxygen have been measured utilizing the resonance reaction $^{18}O(p,\alpha)^{15}N$.

The energy release in this reaction is Q = 3 970 keV. Owing to the negative Q-value of the $^{16}O(p,\alpha)^{13}N$ reaction and the small Q-value of the $^{17}O(p,\alpha)^{14}N$ reaction (Q = +1.19 MeV) there is no interference from these oxygen isotopes. This makes it possible to detect the ^{18}O nucleus in natural oxygen in spite of its low abundance (^{16}O: 99.76 %, ^{17}O: 0.04 %, ^{18}O: 0.204 %). Based on the use of the above reaction many resonances have been reported to be employable for profile analysis. The lowest resonance, at E_p = 629 keV [57], has been found to be very attractive for surface analysis [58]. Since the angular distribution is backward peaked the α-particles were detected at 150°. Introduction of a Mylar foil stops the 0.7 MeV backscattered protons whereas 3 MeV α-particles penetrate and can be detected.

The small width of the resonance (FWHM = 2.5 keV) provides a depth resolutions of 230 Å at the surface and 800 Å at a depth of 0.3 μm. The analysable depth is limited, however, to 2.2 μm as a result of interference from a second, broader resonance at E_p = 830 keV. Nevertheless interference can be avoided, however, by keeping the proton energy so low that the higher resonance is not excited. On the contrary, when the higher resonance is employed the proton energy will always be decreased in thick targets and finally reach the lower resonance energy. This appearently inevitable interference was nevertheless avoided by Price and Bird in the study of

oxygen profiles in titanium and zirconium welds [59]. Discrimination of the alpha energy spectrum was applied so that only 830 keV-resonant α-particles were measured. The actual profile was then studied by moving the sample in lateral directions with respect to the fixed beam. A 50 μm aperture collimated the proton beam on the targets which were studied over a range of some millimeters.

A third resonance in the $^{18}O(p, \alpha)^{15}N$ reaction at E_p = 1 165 keV was used as early as 1962 by Amsel to measure oxygen diffusion profiles in aluminum [25]. Although the extremely small resonance width of 0.1 keV allows a depth resolution of better than 200 Å, the use is restricted to depths of less than 0.5 μm owing to the proximity of other resonances.

On moving to still higher proton energies a sharp increase of the (p, α)-cross-section is reported at E_p = 1 760 keV [60]. This resonance is asymmetric and the analysis of oxygen profiles at these energies is therefore as complicated as those which suffer from multiple resonances and requires a similar procedure.

8 Non-resonant reactions

The principle of the resonance technique applied to profile measurements requires a successive variation of the energy of the incident particle in order to determine the depth. The yield of the emitted particles provides information about the concentration of the studied element present in layers at these various depths.

In non-resonant nuclear reactions the energy of the emitted particle is dependent upon the energy available at the instant of reaction, and this is in turn, related to the kinetic energy of the initial particle. A charged particle continuously loses kinetic energy on its way through matter. Nuclear reactions that are induced by monoenergetic charged particles can therefore be expected to give rise to product particles with different energies, depending on where in the target the nuclear encounter has taken place. In this instance, however, the energy of the emitted particles provides information about the depth parameter, whereas their yield is proportional to the concentration of the element under review within a layer at this depth.

Such methods have obviously the advantage that depth profiles can be obtained in a single run. The result is dependent on the energy of the incident particle only to the extent that the experimental conditions may be optimized as regards desired range and resolution, or signal-to-

noise ratio and the employment of advantageous regions of the cross-section function [61].

Profile measurements by means of non-nuclear reactions

From the review of the literature it is obvious that methods which are based on Auger-electron spectroscopy or X-ray excitation are not specially suited to the measurement of chemical profiles. As regards depth determination these techniques are only semi-quantitative in character. The depth parameter is determined either by controlling the sputtering rate [e.g. 62] or by the energy-range relationship for the incident particle together with estimates of the production and attenuation of the emitted X-radiation [e.g. 63]. In both cases the ranges over which profiles can be studied extends to ~ 1 000 Å. Many authors claim that depth control applied in sputtering is accompanied by large uncertainties. These may arise from the creation of non-planar surfaces during ion bombardement and from the deformation of the profile due to head-on collisions.

A new approach has been reported by Pabst [64]. He made use of the variation of the X-ray yield as a function of the tilting angle of the target in order to unfold the yield spectra obtained from thick target irradiation. It seems to be difficult to make an exact profile determination owing to the uncertainties in the data used and to oscillations in the adopted smoothing function. However, it was possible to obtain a profile for Te atoms in a InSb matrix over a range of 2.5 μm. The total uncertainty of the method, however, is not reported.

The use of Rutherford scattering for profile measurements has been successfully tested in many laboratories and it is to date a well established technique. The typical application of Rutherford scattering in analytical work is the determination of heavy elements in a light matrix. The one-to-one correspondence between the energy of the scattered ion and the depth of collision for a given scattering atom makes possible the measurement of depth profiles. In this sense dynamical processes such as diffusion can be studied by consecutive measurements on thermally treated samples. An example of this approach is the investigation of the diffusion of heavy metals in silicon using 2 MeV He^+ backscattering [65]. The results obtained suggested that some metals (Fe, Co and Au) are gettered slowly, whereas others (Cu and Ni) are removed more rapidly from ion-damaged surfaces.

Backscattering has been used successfully for the investigation and localization of low-concentration, high Z impurities in semiconductor material.

The introduction of the channeling technique permitted both the sensitivity and the range of the backscattered ions to be increased appreciably. Depth distribution in three dimensions could now be studied and distinction made between foreign atoms on lattice sites and those present in interstitial positions [e.g. 66].

Contrary to the trend, whereby Rutherford scattering is applied to the detection of heavy atoms in light matrices, a very elegant experimental study concerning the depth distribution of hydrogen in metal matrices, has been reported by Cohen et al. [67]. Thin targets of Ti, Zr, Al and Fe were used and hydrogen was detected by proton-proton forward scattering at 17 MeV. The speciality of the technique was to make use of the fact that a hydrogen atom and a proton have identical mass. Both nuclei are observed at an angle of 45° with respect to the incident proton beam. Thus for the momentum and energy to be conserved the energy of the scattered hydrogen atom must be identical to that of the scattered proton. Both particles can thus be detected using time coincidence technique. On penetrating the matrix both the incident and the scattered protons lose energy. Owing, however, to the non-linearity of the stopping power as a function of energy the scattered proton loses more energy per depth interval than the incident proton. The arising difference can be measured in the energy spectra of the particles and this parameter provides information about the depth of the scattering position.

This method is only applicable to thin targets (50-120 μm foils were used), that are transparent to the protons. As a result of the energy-, time- and angle-requirements imposed on the detected events, the above described technique exhibits a sensitivity of 1 ppm for hydrogen concentrations in metals. The spatial resolution has been determined to be about 3 Å at the surface of the specimen. At greater depths resolution deteriorates owing to multiple scattering effects.

Helium is another light element that has been studied in a heavy matrix using Rutherford backscattering. According to Bragg's additivity rule the stopping power in a solid increases with the amount of light impurities present. A concentration profile of helium ions implanted in polycrystalline niobium was therefore determined by measuring the variation of the stopping

power with depth for 150 keV protons [68]. The energy spectra due to backscattered protons from polycrystalline niobium were compared to those from a niobium single crystal measured under identical experimental conditions. The energy resolution afforded by this technique was determined to be 3 keV, which corresponds to 50 Å.

The purpose of the measurement was to obtain concentration profiles for 4 keV He^+-ions implanted at different temperatures. It was found that the profiles flattened with increasing target temperature, and a considerable amount of helium was found at depths beyond the range of He-ions. Although it is known that Bragg's rule slightly overestimates the concentrations of the different components the results are believed to be reproducible to within 20 %.

Profile measurements by means of nuclear reactions

As mentioned earlier the principle feature of the non-resonant method is depth determination by analysis of the energy spectra of the emitted particles. It is therefore surprising to find this method applied to a reaction, in which the emitted radiation are γ-rays [69]. In general the emission of γ-rays is a strongly resonant phenomenon. It was found, however, that the energy of the γ-rays emitted from the 0.6 MeV-level in the residual nucleus of the $^{16}O(p,\gamma)^{17}F$ reaction is linearly dependent on the proton energy, given by $E_\gamma = 0.600 + 16/17\ E_p$. The signal-to-noise ratio can be increased by applying coincidence technique, since the γ-rays concerned are emitted in cascade. Although the method has been proposed for the direct determination of thin oxide layers nothing is known about the sensitivity or time requirement for such a measurement.

Energy spectra of charged particles

A variety of charged particle induced techniques for the study of depth profiles are described in the very comprehensive and instructive review compiled by Wollicki [70]. Owing to the low Coulomb barrier for nuclei with low atomic numbers nearly all the light elements, especially in heavy matrices, can and have been studied by using non-resonant reactions.

Of the light elements concerned oxygen is the one most often measured. (See Table I). The study of the diffusion of oxygen in quartz using the already mentioned $^{18}O(p,\alpha)^{15}N$ reaction has become a classical

example [71]. In this instance the profile was established, not by employing a resonance, but by the analysis of the energy spectrum of the α-particles emitted for an initial proton energy of 500 keV. The instrumental resolution, ignoring straggling effects, was reported to be about 0.25 μm and diffusion profiles were studied within a layer 2 μm thick.

In view of the large cross-sections in ^{3}He and ^{4}He induced reactions, use has even been made of ^{17}O as a tracer for oxygen profile measurements, utilizing the reaction $^{17}O(^{3}He, \alpha)^{16}O$ [72]. The Q-value of this reaction is favourably high (16.43 MeV) and provides the α-particles with an energy which is higher by 3 MeV than those produced in the reaction $^{18}O(^{3}He, \alpha)^{17}O$. However, α-particles produced in the reaction with ^{13}C generate interference so that the effective range is reduced to 5 μm.

While it is clearly advantageous to measure α-energy spectra in view of the superior resolution obtained the total ranges are correspondingly short. A representative example of this topic is provided by the recent work of Turos et al. [73]. Oxygen profiles in oxide layers of thicknesses between 0.2-1.2 μm thermally grown on silicon were studied employing the $^{16}O(d, \alpha)^{14}N$ reaction. The resolution obtained was 0.02 μm. They also discuss optimization of the method according to the choice of detector (sensitive zone), of the angle of detection and of the incident energy. The profiles obtained have been compared with assumed shapes that were convoluted with the appropriate resolution function. When agreement is obtained between the experimentally measured profile and the result obtained by convolution the initial constructed shape describes the "real oxygen distribution".

The reason for the short range of these techniques is the fact that both the incident and the emitted particle suffer from energy degradation in connection with the penetration of the matrix. Thus for thick targets only back-angle detection can be employed.

Energy spectra of neutrons

Many of the problems involved in the techniques that utilize detection of an emitted charged particle are circumvented, if not eliminated, by measuring the energy spectrum of neutrons. Microanalysis has been carried out using (d, n)-reactions in combination with neutron-time-of-flight technique on light elements in metal surfaces [74] and in gases [75]. Detection limits of the order of 0.1 μg/cm^{2} have been reported. In the investigations

of Möller and co-workers the possibility of extending the analytical (d, n)-method to the measurement of depth profiles in metal surfaces was pointed out.

The feasibility of this method has been studied systematically and is described in Paper IV. Concentration depth distributions of carbon and nitrogen in steel and diffusion profiles of oxygen in zirconium matrices have been measured. The samples were irradiated with a pulsed deuteron beam at energies lying between 2.5 and 5 MeV. The neutrons emitted in the corresponding reactions were measured at optimized forward angles of 0° and 20° using time-of-flight technique. An appreciable part of the background due to γ-radiation from deuteron activated material is reduced by applying n-γ-discrimination. Low deuteron currents (below 1 μA) were applied in order to avoid destructive thermal effects in the targets during the 10-min irradiations.

In this work a fast method for the analysis of elemental concentration profiles is described. This is based on the comparison of the neutron energy spectra produced by gradients (i.e. inhomogeneous elemental distributions) to those obtained from homogeneous standards, measured under identical experimental conditions. The channel-by-channel ratio of the equivalent spectra provides the final depth distribution of the three elements carbon, nitrogen and oxygen studied. The generation of the ratio function R(x) of the depth x renders the exact knowledge of the shape of cross-section and of the efficiency of the neutron detector unnecessary. On the other hand, a procedure has been developed which allows to optimize the choice of the deuteron energy, based on the qualitative knowledge of the cross-section and efficiency function. The concentration profiles obtained by this technique are in satisfactory agreement with the results obtained on applying the resonance method for carbon and microscopical studies for oxygen.

The technique thus developed appears to be particularly suited to the investigation of oxygen diffusion profiles in view of the best resolution that can be obtained for the three elements studied. Concentration profiles have been measured over a range of 10-15 μm in a single run with depth resolutions of 0.5 to 1 μm, including straggling effects. The zirconium samples used were specially treated in order to simulate corrosion on fuel cladding material for reactor purposes. Variations of the oxide thickness in the specimen surfaces and of the shape of the diffusion profiles, produced

by heat treatment of the samples at different temperatures between 700°C and 1 200°C, are clearly demonstrated.

Further application of this method to the investigation of dynamical processes, such as the growth of oxide films under stable thermal conditions, is projected in order to increase the knowledge about corrosion. In this way macroscopical, destructive, neutron-induced reactions might be studied with the help of microscopical, non-destructive, charged particle-induced reactions.

ACKNOWLEDGEMENT

The experimental work described in this thesis has been performed at the Van de Graaff laboratory of the Atomic Energy Company in Studsvik. It is a pleasure to acknowledge the support given by the head of this institution, Prof G Holte, and the heads of the Section for Nuclear Chemistry, Fil lic G Carleson and of the Section for Neutron Physics, Dr T Wiedling.

I am greatly indebted to Dr D Brune, who introduced me to the problems of profile measurements and for his guidance and encouragement throughout this work, and it is with pleasure that I express my gratitude to Dr S Malmskog for stimulating co-operation and for his invaluable help in many discussions.

Special thanks are extended to the members of the accelerator group for their considerable technical help. I also want to thank the personnel of the Studsvik library and of the secretarial department for their rapid assistance.

I am very grateful to Fil lic A Brown for his untiring efforts in correcting the manuscript and to Dr B Holmqvist for his careful reading and constructive criticisms.

Finally I wish to thank all my colleagues and friends for their openminded readiness and moral help.

The work was financially supported by the Swedish Board of Technical Development.

Table I

Nuclear reactions used for depth distribution measurements of oxygen

Reaction	Range (μm)	Resolution (Å)	Q-value (MeV)	Incident particle energy (MeV)	Resonance energy (keV)	Resonance width (keV)	Angle of detection	Enriched target	Ref
$^{16}O(d,p)^{17}O$	5	2 500	1.05	0.9	-	-	165°	no	[57]
$^{16}O(d,\alpha)^{14}N$	1.5	400	3.115	0.9	-	-	145°	no	[73]
$^{16}O(d,n)^{17}F$	15	4 500	- 1.627	3.5	-	-	0°	no	present work
$^{17}O(^{3}He,\alpha)^{16}O$	3.5	1 200	16.435	5.3	-	-	90°	50 %	[72]
$^{18}O(p,\alpha)^{15}N$	3	2 500	3.970	0.5	-	-	150°	-	[71]
$^{18}O(p,\alpha)^{15}N$	< 1	150	3.970	0.6	-	-		94.5 %	[76]
$^{18}O(p,\alpha)^{15}N$	0.3	60-200	3.970	0.6	-	-	165°	92.5 %	[57]
$^{18}O(p,\alpha)^{15}N$	2.2	230	3.970	0.63	629	2.5	150°	10 %	[58]
$^{18}O(p,\alpha)^{15}N$	$>10^{3}$*	$5 \cdot 10^{5}$*	3.970	0.87	845	40	90°	no	[59]
$^{18}O(p,\alpha)^{15}N$	0.5	200	3.970	< 2	1 165	0.1	170°	90 %	[25]
$^{18}O(p,\alpha)^{15}N$	~ 2	~ 800	3.970	2	1 760	32	176°	-	[60]

* Scanning technique

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Abstracts of Uppsala Dissertations from the Faculty of Science
Editor: The Dean of the Faculty of Science

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ISBN 91-554-0263-1