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Determination of the Mg-Concentration Profile in Near-Surface Layers of Materials Using the $^{24}Mg(\alpha,p)^{27}Al$ Nuclear Reaction

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Abstract. The $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction was applied for the determination of the magnesium distribution in near-surface layers of materials. The cross sections of this reaction were determined in the energy region between 4.5 and 5.5 MeV in steps of 5 to 10 KeV (θ_{lab}: 158°) using thin magnesium films. The investigated projectile energy region included five main resonances allowing the determination of magnesium. The uncertainty of the cross-section determination was of the order of 7%. The applicability of the technique was tested using Mg-implanted AISI 321 steel samples. Depth resolution of 100 nm and detection limits of the order of 0.1 ppm were achieved for the determination of magnesium in steel samples using the 4805 keV resonance of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction. The shape and height of the magnesium depth-profile in the Mg-implanted steel samples were compared with corresponding values obtained by X-ray photoelectron spectroscopy.

Key words: Ion-beam analysis; magnesium; nuclear reactions; cross-sections.

Magnesium is an element of considerable significance in materials technology. Small amounts of this element can be found as minor constituent of aluminium matrices and in composite materials [e.g., 1–3]. Despite the fact that magnesium is electrochemically the most active of the metals used as commercial engineering materials, it found a number of applications as constituent of metallic alloys providing good atmospheric corrosion resistance [e.g., 4–6]. Magnesium implantation of stainless steels has also been investigated in an attempt to improve their oxidation resistance [7–8].

The determination of the depth distribution of magnesium in near-surface layers of materials can be mainly performed using nuclear reaction and scattering analysis techniques [e.g., 9–10]. Since the determination of low magnesium concentrations in heavy matrices by Rutherford backscattering spectrometry (RBS) is frequently connected with certain difficulties, the utilization of prompt particle spectrometry selecting an appropriate nuclear reaction remains the most suitable technique for this purpose. Olivier and Peisach [11] used a deuteron microbeam and prompt proton spectrometry utilizing (d,p)-type nuclear reactions for the determination of the magnesium distribution in Mg-rich aluminum alloys, whereas Colin et al. reported on the use of ^{15}N-ion beams for the determination of magnesium in alumina powders [12]. On the other hand Noli et al. [7–8] used the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction along with ^{4}He-RBS and X-ray photoelectron spectroscopy (XPS) for the determination of the magnesium distribution in near-surface layers of Mg-implanted AISI 321 stainless steel samples before and after thermal treatment at high temperatures. The excitation function of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction possesses a number of resonances [13], that can be utilized for this purpose.

The aim of the present work was to determine the cross-sections of the $^{24}Mg(\alpha,p)^{27}Al$ reaction in the energy region between 4.5 and 5.5 MeV required for

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the absolute quantitative determination of magnesium in near-surface layers of materials without utilization of reference materials.

Experimental

The measurement of the cross-sections of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction was performed using the α-particles beam of the 7 MV van de Graaff accelerator of the Nuclear Physics Institute of the University of Frankfurt/Germany. The irradiation chamber was carefully insulated from the rest of the equipment and could be used as Faraday cup. The surface barrier detector used for the detection and counting of the protons emitted by the above nuclear reaction was positioned at a laboratory angle (θ) of 158° with respect to the incident beam facing the target with a solid angle ($\Delta\Omega$) of 3.0 msr. Mylar foils (density: 1.397 g/cm^3, thickness: 10 μm) were placed in the front of the detector in order to stop the backscattered α-particles. The total charge of the beam was 10 μCb corresponding to 6.25×10^{13} incident particles. The precision of the current measurement, including the quality of the current integrator and the insulations of the Faraday cup, was ca. 5%. The beam energy was varied between 4500 and 5500 keV in steps of 5 keV in the resonance and 10 keV in the off-resonance region, respectively. Target deterioration tests were performed before and after irradiating the same target point in order to investigate the beam-induced alteration of the target. These measurements were performed by Rutherford backscattering spectrometry (RBS) using 2 MeV $^4He^+$-particles. For the counting of the backscattered α-particles a surface barrier detector was positioned inside the irradiation chamber at an angle of 171° to the beam direction. However, in order to avoid discrepancies due to the target deterioration each target was maximally irradiated with a beam charge of 70 μCb.

Two types of targets were used for the experimental work. The first type of targets was prepared by the Sample Preparation Group at the Institute for Reference Materials and Measurements (IRMM, Geel/Belgium) using vacuum deposition of MgF_2 (chemical purity 99.99%) on polished tantalum substrates. The mass thickness of the deposited material was 30 ± 0.5 μg/cm^2 determined by quartz monitoring. The energy loss of 5.0 MeV α-particles in these targets was calculated by the Monte-Carlo code TRIM [14] and found to be 20 keV. Furthermore, thinner Mg-targets were prepared by implantation of 40 keV Mg-ions in carbon foils in order to obtain a better resolution. The implantation was performed using the 50 kV ion-implanter of the Nuclear Physics Institute of the University of Frankfurt/Germany. To avoid the surface contamination of the samples by hydrocarbon vapor deposition in the implantation chamber, a liquid nitrogen trap was surrounding the target arrangement during the implantation. The vacuum in the chamber was better than 10^{-4} Pa. The thickness of the implanted region, measured by $^4He^+$-RBS ($E_\alpha = 2$ MeV, $\theta = 171°$), was found to be 1.8×10^{17} Mg-ions/cm^2 corresponding to ca. 41.5 nm. The evaluation of the RBS spectra was performed by simulation using the computer code RUMP [15]. The energy loss of the 5.0 MeV α-particles in these targets, also calculated by the code TRIM, was found to be 5 keV.

In order to demonstrate the suitability of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction for the determination of the magnesium distribution in the near-surface layers of materials, Mg-implanted steel samples were prepared by ion-implantation. 2×10^{17} Mg ions/cm^2 of 40 keV energy were implanted on mechanically polished AISI 321 stainless steel (Fe/Cr18/Ni8/Ti) samples (dimensions: 1.2×2.5 cm^2, thickness: 0.25 mm, supplied by Goodfellow). The implantations were also performed using the already mentioned implanter facilities of the University of Frankfurt/Germany.

The magnesium distribution in the near-surface layers of the Mg-implanted steel samples was also determined using X-ray photoelectron spectroscopy (XPS) at the École Nationale Supérieure de Chimie de Toulouse, France. An ESCALAB MARK 2 VG instrument equipped with a Mg-K_α source was used for these measurements. The source was run at 300 W and the emitted photoelectrons were sampled from an area of 1 mm^2. A 100 μA Ar^+-beam of 4 keV energy was utilized for the erosion (sputtering) of the surface layers of the samples.

Results and Discussion

The Q-value of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction is -1.6 MeV [13] and the energy of the emitted protons is 2081 keV for E_α 4800 keV. The energy loss of the protons of the above energy in Mylar is ca. 21 keV/μm. Figure 1 gives the experimental cross-sections of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction as a function of the incident proton beam energy. The measurements obtained for the laboratory angle (θ) of 158° using the thick Mg-targets. The cross-section values ($\sigma(E,\theta)$) presented in this figure were calculated using the following formula [16]

$$\frac{d\sigma(E,\theta)}{d\Omega} = \frac{Y(E,\theta)}{N_p \times N \times \Delta\Omega}$$

where N_p, N, $Y(E,\theta)$ and $\Delta\Omega$, respectively, represent the number of projectiles, the number of Mg-atoms (target atoms) per unit of surface, yield of the promptly emitted protons and solid angle.

The cross-sections obtained using the thin Mg-implanted targets reproduced the width and the form of the resonances measured by the thick targets as it is

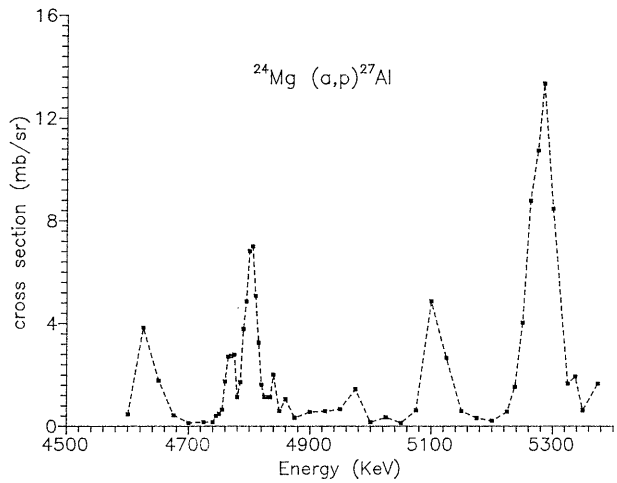

Fig. 1. Cross sections of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction as a function of energy at 158° in the energy region 4600–5400 keV using thick Mg-targets

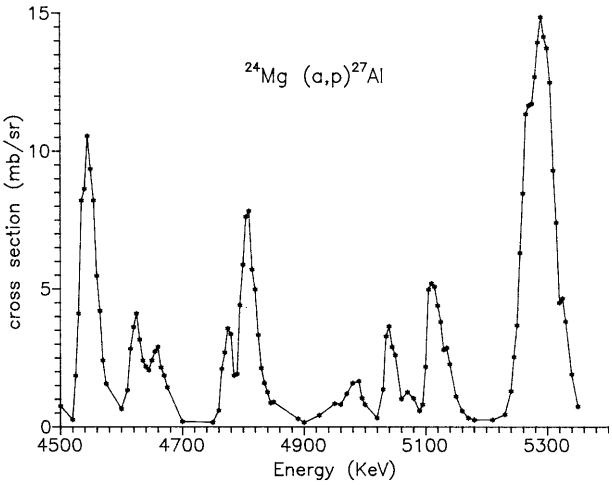

Fig. 2. Cross sections of the $^{24}Mg(\alpha, p)^{27}Al$ nuclear reaction as a function of energy at 158° in the energy retion 4500–5400 keV using thin Mg-targets

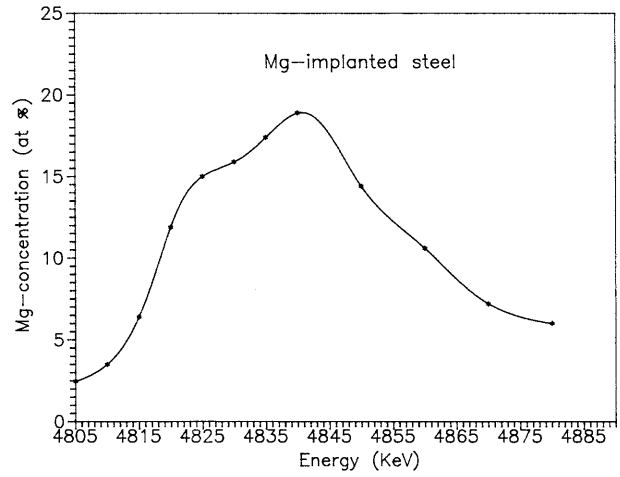

Fig. 3. Distribution of magnesium on an AISI-321 stainless steel sample implanted by 40 keV Mg-ions determined by means of the $^{24}Mg(\alpha, p)^{27}Al$ nuclear reaction (The energy of 4805 keV corresponds to a layer of 0 nm thickness as well as the energy of 4880 keV corresponds to a layer of ca. 70 nm thickness)

shown in Fig. 2, offering a better resolution. These measurements allowed the observation of several resonances in the investigated projectile energy region (4545, 4805, 5040, 5110 and 5290 keV respectively), that could be utilized for the determination of magnesium in near-surface layers of materials. The distinction of the individual resonance peaks in the prompt-proton spectrum at energies higher than 5400 keV was impossible, because of the high background.

Of special interest for the magnesium determination are the resonances at 5290 (FWHM: 47 keV) and 4805 keV (FWHM: 31 keV). The first of these resonances has considerably high cross-sections allowing the determination of low concentrations of magnesium, whereas the second one has lower cross-sections but smaller width providing higher depth-resolution. Both resonances are preceded by a low cross-section non-resonant region enabling the probing of near-surface layers of materials of considerable thickness avoiding the interference of lower-energy resonances. The presence of the low-energy satellite of the 4805 keV resonance at 4770 keV does not seriously interfere the determination of the magnesium distribution because of its lower cross-section values and smaller width (ca. 20 keV). The resonance at 4545 keV has almost the same width as the resonance at 4805 keV but is followed by another resonance at 4625 keV making the Mg-profiling in thicker targets rather complicated.

The applicability of 4805 keV resonance for the Mg-concentration profile in near-surface layers of materials was demonstrated using Mg-implanted steel samples. For these measurements the target was mounted at an angle of 74° to the beam direction in order to increase the apparent thickness of the Mg-containing layer traversed by the projectiles and consequently obtain a better depth resolution of the determination. Figure 3 gives the experimentally determined Mg-distribution in AISI-321 stainless steel sample implanted with 2×10^{17} Mg-ions/cm^2 (implantation energy 40 keV), whereas Fig. 4 gives the theoretically expected distribution calculated by the computer code TRIM.

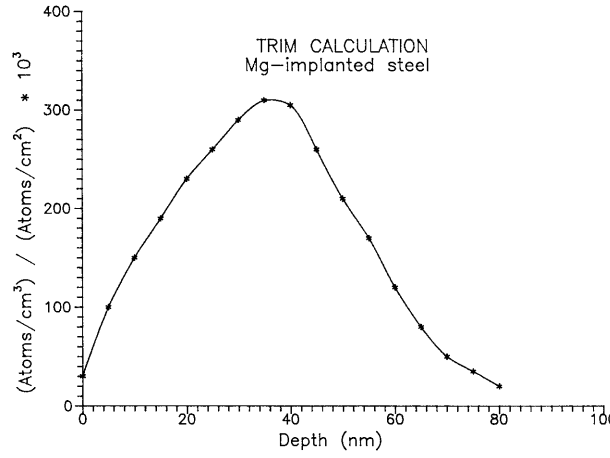

Fig. 4. Theoretical calculation of the Mg-profile on AISI-321 stainless steel using the computer code TRIM

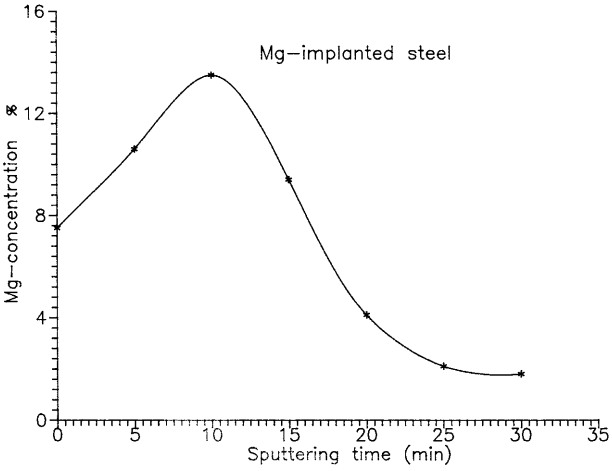

Fig. 5. Distribution of magnesium on a Mg-implanted AISI-321 stainless steel sample (implantation energy: 40 keV) using XPS. The total sputtering time on this graph corresponds to a layer of ca. 60 nm thickness

The energy loss (dE/dx) of α-particles of energies 4.5 to 5.0 MeV in the Mg-implanted steel was calculated to be 290 to 310 keV/μm (TRIM calculation) and their range ca. 70 nm. Taking into account the above results the mean range of the distribution ($E = 4840$ keV) in Fig. 3 corresponds to ca. 32 nm as well as the maximum distribution range ($E = 4880$ keV) to ca. 70 nm. The conversion of the projectiles energy to depth in Fig. 3 was performed using the formula [16]

$$E_0 = E_R + \left(\frac{dE}{dx}\right)_{in} \times \left(\frac{x}{\cos\theta}\right)$$

where E_0, E_R, $(dE/dx)_{in}$, x and θ are respectively the incident beam energy, the resonant energy, the stopping power of incident beam, the depth and the angle between the incident beam and the target surface.

As expected, the magnesium distribution has the shape of a Gaussian with the concentration slowly tailing-off into the metal. The slight difference between the experimental (Fig. 3) and the theoretical values (Fig. 4) is probably due to sputtering effects and to expansion of the structure because of the implantation.

These results of Mg-determinations in Mg-implanted steels indicate, that, when the resonance at 4805 keV is completely inside the target, a depth-resolution of ca. 100 mm in steels can be achieved. The lower detection limit of the determination was estimated to be around 2.8×10^{15} Mg-atoms/cm^2 (ca. 0.1 ppm).

For comparison reasons the magnesium depth-distribution on the same Mg-implanted steel samples was determined by XPS (Mg1s $E = 1305$ eV). A sputtering time of 5 min on the surface of the steel sample, using 100 μA Ar^+-beam of 4 keV energy, corresponds to a layer of ca. 10 nm thickness. The results of this measurement are presented in Fig. 5. The shape and the height of the distribution are in good agreement with the results obtained using the 4805 keV resonance of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction and the cross sections determined during this work.

Conclusions

The resonances of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction at 5290 and 4805 keV can be successfully applied for the determination of the magnesium in near-surface layers of materials without serious interference from neighboring resonances. Especially useful for this purpose is the resonance at 4805 keV energy (FWHM: 30 keV), which leads to depth resolution of ca. 100 nm in steels. The absence of background in this region of the emitted proton spectrum allows the determination of Mg-concentrations of the order of 2.8×10^{15} at/cm^2 (ca. 0.1 ppm). The uncertainty of the cross-section values for the resonances of the $^{24}Mg(\alpha,p)^{27}Al$ nuclear reaction determined during this work is ca. 7%.

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