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Application of Positron Annihilation Spectroscopy to Studies of Subsurface Zones Induced by Wear in Magnesium and its Alloy AZ31

Jerzy Dryzek¹ and Ewa Dryzek²

¹*Institute of Physics, Opole University, ul. Oleska 48, 45-052 Opole*

²*Institute of Nuclear Physics PAN, ul.Radzikowskiego 152, 31-347 Kraków
Poland*

1. Introduction

Interaction of sliding bodies is an important aspect of numerous applications and subject of many studies (Solecki, 1989). Generally, when two surfaces are loaded together the true contact area is much smaller than the apparent one. The true contact is only at high points or asperities of the surfaces where the interactions in the atomic scale take place. Relative movement between the surfaces leads to friction and wear processes. The rate of wear is controlled by the load, the relative velocity and the behaviour of the material near asperities. The region of asperities can be plastically deformed and the stress is transported to the deeper laying region that becomes elastically deformed (Fig. 1).

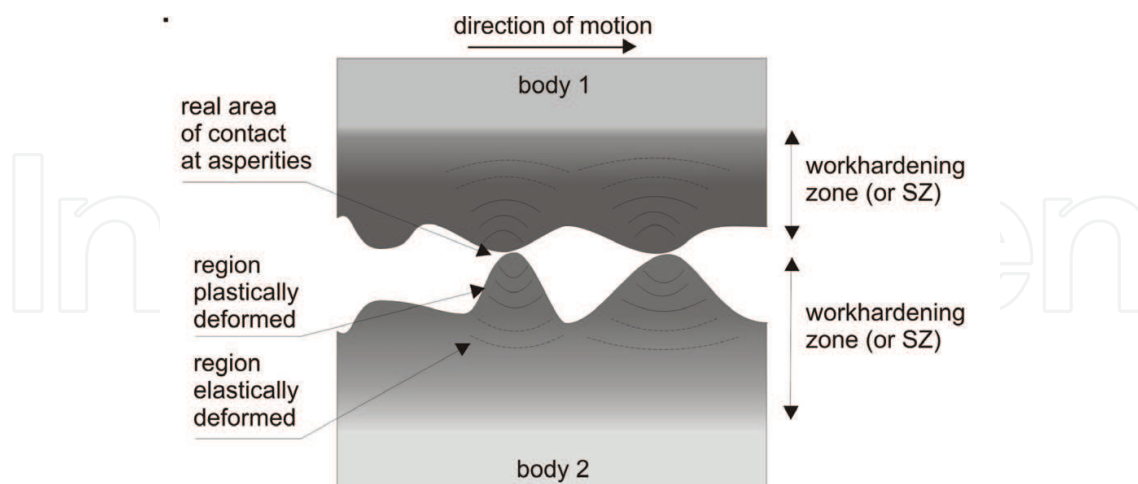


Fig. 1. Schematic diagram of the contact of two metal surfaces. The SZ is denoted as a dark grey area.

A composition and physical properties of the subsurface zones are substantially modified in comparison to those of the bulk (Wert, 1989), (Rice et al., 1989). The outermost zone contains original specimen material but also chemical species from the counterface and from the

environment, e.g. adsorbed polar particles, water, gases and oxides. Usually, it appears homogeneous and has very fine structure. Its boundaries may be confirmed by elemental analysis. In case of metals this zone is from 10 nm to 20 nm thick. Underneath, there lays the zone consisting entirely of the original specimen material but it is heavily plastically deformed. The zone acquired new structure and properties due to the repetitive tribocontact, e.g., it may become usually harder than the original material. Usually, there are the reorientation and disintegration of crystallites in it. The next zone represents the original specimen material in an undisturbed state. This zone experiences elastic deformation. However, its structure and properties are identical to those prior to the tribotest. It is accepted to call the region below the worn surface the subsurface zone (SZ), which was induced by the friction process. It seems that this zone reflects all the processes which occur at the worn surface and can be a key to the understanding of the wear process.

The SZ can be studied by different methods. The residual stress depth distribution or the microhardness profiles are the common engineering methods. For detail studies the electron microscopy techniques or XRD techniques are applied. The positron annihilation spectroscopy is also used for studies of the SZ. It offers a possibility of detecting and distinguishing between open-structure crystal defects such as dislocations, vacancies, and voids in metals. All they are induced by any deformation of the material.

2. Brief review of positron techniques

The positron is an antiparticle of the electron; their interaction may cause the transformation of their mass into the electromagnetic radiation called annihilation rays. The main process (99.8% probability) is emission of two photons. Their detection is the base of the positron annihilation spectroscopy. The sources of positrons are mainly isotopes emitting positrons via β^+ decay, ^{22}Na and $^{68}\text{Ge}/^{68}\text{Ga}$ are commonly used in the solid state studies. Positrons emitted in β^+ decay have a continuous energy spectrum what means that its energy can be in a range limited by a maximum energy characteristic for the isotope. Positrons from the radioactive source cannot be implanted into a solid at a strictly defined depth. Typical implantation ranges characterized by linear-absorption coefficient are of the order of a few tenths of millimeter and depend on the density of the solid and the atomic number (Dryzek, Singleton, 2006). (The reciprocal of the so called linear-absorption coefficient for magnesium is equal to 144 μm for positrons emitted from ^{22}Na , and this quantity can be treated as the implantation range.) Hence, the positron as a probe penetrates certain, relatively large volume in the atomic scale. It should be noted that the positron beam technique allowing to implant positrons of low energy into a defined depth at the range of micrometers are in use (Krause-Rehberg & Leipner, 1999).

As a charged particle, a positron injected into a solid interacts inelastically and elastically with other charged objects, i.e., electrons and nuclei, and loses rapidly its kinetic energy until it becomes thermalized. Being in a thermodynamic equilibrium with the host, the positron is scattered by phonons and walks randomly. The random walk lasts much longer than the thermalization process, i.e. between 100 ps and 500 ps. It is sufficient for a positron to penetrate the volume occupied by ca. 10^7 atoms, mainly interstitial regions in the host lattice, before it annihilates with the emission of two almost collinear photons in opposite directions with of energy about 511 keV, Fig. 2. The positive charge of the positron causes that it annihilates mainly with the valence or conduction electron. The probability of the annihilation with the core electrons is much lower.

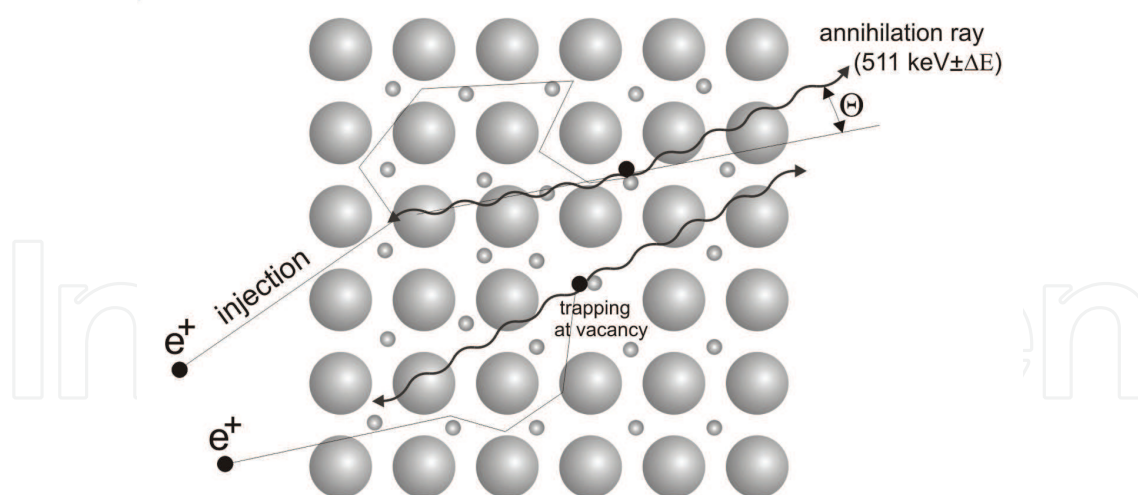


Fig. 2. The positron paths in a metal crystal lattice. Positron moves across interstitial regions between the ions or atoms (big grey spheres) and finally finds an electron (small grey spheres). In some cases it can be trapped at a vacancy or other open volume defect of crystalline lattice. ($\Delta E = p_z c / 2$, $\Theta = p_{x,y} / (m_0 c)$, where $p_{x,y,z}$ are the components of the electron momentum, m_0 is the electron rest mass and c is the speed of light.)

The positron during its diffusion can be trapped in regions of lower than average electron density like vacancies, vacancy agglomerates, dislocations, microvoids or small pores if they exist. They are defects of the crystalline lattice. The localization in such regions is due to the repulsion between the positron and the positive atomic cores. It is easy to distinguish where the annihilation takes place. Electrons in the interstitial regions have higher momentum than those in the vacancy-type defects, thus the total momentum of the emitted photons tags these annihilation places. Due to the thermalization the momentum of the positron can be neglected but the electron momentum cannot. The measurement of the deviation from the co-linearity of the two photons, the angle θ in Fig.2, is the simplest way to deduce the total momentum of the annihilating pair, it means the electron. Another method is the measurement of the Doppler broadening of the annihilation line which is also sensitive to the momentum of the annihilating electron. The vacancy-type defect, which traps positrons, contains fewer electrons than the interstitial regions; it causes the significant change in the annihilation rate. In other words, the annihilation in the lower-electron density region induces the increases of the positron lifetime. Indeed, the positron lifetime, i.e. the time interval between the “birth” of a positron and its annihilation, is larger for positrons localized in defects than in the interstitial. As it was stated above the time of implantation is much smaller than the time of random walk. The theoretical calculations supported by numerous of experimental results show additionally that the average lifetime of positrons localized in small vacancy clusters is very sensitive to their size. Hence, the identification of the kind of the trap: single vacancy or a multiple vacancy is possible. In magnesium, the mean bulk lifetime of positrons is equal to 225 ps, while the lifetime of positrons trapped at vacancies in this metal is 253 ps. For the measurement of the positron lifetime, the isotope ^{22}Na is usually used as a positron source. After emission of the positron, the gamma photon of energy 1275 keV is emitted from the excited state of the ^{22}Ne . This photon tags the “birth” of the positron and the emission of the annihilation ray tags its “death”. The time between both events is simple to measure using a typical spectrometer and

it is equal to the positron lifetime in the implanted sample. The positron lifetime spectroscopy is a powerful tool for studies of condensed matter at atomic level (Brandt & Dupasquier, 1983).

3. Studies of the SZ by positron techniques

There are several advantages of this technique in comparison with the transmission electron microscopy. The positron as a probe can be implanted from external source into a sample which does not need any special treatment. The measurements are non-destructive using samples as they are. Only a pair of relatively flat samples treated in the same way is required to sandwich a positron source. The examples of the use of this technique for studies of vacancies, dislocations, fatigue damage, hydrogen trapping, and SZ do not exhaust the list of possible applications (Dupasquier & Mills, 2004). The disadvantage is the fact that positrons are mobile particles and scan relatively large volume of the sample before annihilation. For that reason positron annihilation can be used for studies of the whole SZ.

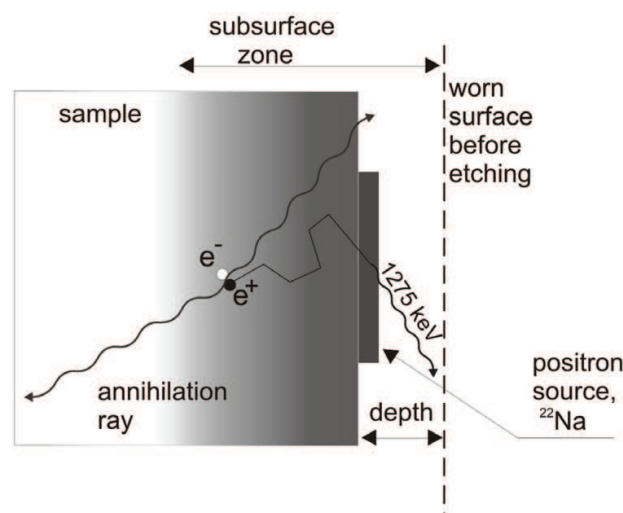


Fig. 3. A positron path in the sample. The positron is emitted from the ^{22}Na isotope which is located on the surface. The depth marked in the figure, represents the thickness of the layer etched from the worn surface. (In the typical experiment the identical sample is located also on the right side of the positron source. It is not shown in the figure for simplicity.)

It is known that after dry sliding of a ductile sample against a harder counterpart the plastically deformed layers occur below the surface. According to some models and a transmission electron microscopic studies that layers contain mainly dislocations and dislocation cells (Hirth & Rigney, 1976). Motion of dislocations induced by plastic deformation accompanying sliding contact generates large amount of point defects. Thus, dislocations can be associated with the point defects, like vacancies or interstitial atoms (Hull, 1975). Vacancies, due to their mobility at room temperature or temperature induced by sliding treatments, can join together and form vacancy clusters. The dislocation network can be studied directly by TEM. In general, detection of vacancies and small vacancy clusters using this method is more challenging task. Similarly, the microhardness profile measured in the SZ gives information on work hardening connected to a large extent with increase of dislocation density. As was mentioned above positrons are very sensitive and unique probes for point defects such as vacancies and vacancy clusters, and also dislocations. (It should be mentioned that interstitial atoms are not detected by positron techniques.) Additionally, detection of the depth profile of

the defect concentration and hence the detection of the SZ induced by the surface treatment may be performed. A great amount of point defects like vacancies associated with dislocations (in aluminum) (Dryzek & Dryzek, 2004) or vacancy clusters (in copper) (Dryzek & Polak, 1999) was found below the worn surface using this method. Their concentration decreased with depth and reached the bulk value at a depth of hundreds of micrometers. The limited implantation range of positrons from ^{22}Na gives the opportunity to determine the total range of the crystal lattice changes induced by friction and wear. In order to do it, the technique based on the sequenced etching of the layers from the worn surface and measurements for instance the positron lifetime was proposed, Fig. 3 (Dryzek et al., 1997). It allows us to scan the depth of the sample from the worn surface. That technique is very efficient, because due to the great sensitivity of the positrons to the open volume defects it allows us to detect the total range of the SZ even the regions where only elastic deformation took place. The relatively simple experimental procedures and high sensitivity exceed the electron microscopy techniques, XRD and another engineering technique, i.e., microhardness measurements.

As it was mentioned already the thermalized positrons penetrate the large volume of the sample. Additionally, the implantation profile of energetic positrons exhibits the exponential decay with the maximal value at the surface (Dryzek & Singleton, 2006). In case of magnesium the depth of implantation range of the positrons emitted from the ^{22}Na isotope is about 144 μm , it means that about 63% of the positrons are located in the layer of such a thickness. From that reason it is difficult to define the exact current depth where the positrons are implanted. In our measurement procedures we trace the dependencies of the positron lifetime as the function of the etched layer thickness, called "depth", Fig. 3.

4. Studies of the SZ in pure magnesium

The success of the positron annihilation techniques in studies of the SZ in pure copper and aluminium encourages us to extend their application for studies of the SZ generated during friction in pure magnesium and its selected alloy. It is commonly accepted that the microstructural parameters, the crystal structure, degree of chemical order, the grain boundaries, stacking faults and the precipitations influence the plastic deformation and fractures.

4.1 The SZ detected by conventional positron technique

Magnesium has a close-packed hexagonal crystalline structure, low strength and high damping due to the easy motion of dislocations at room temperature. As a hexagonal metal with $c/a > 1.633$ magnesium has only three independent slip systems which may occur on either non close packed planes or in non close-packed direction. The main deformation mode is a basal slip, i.e. a slip on the (0001) plane with a $(11\bar{2}0)$ Burgers vector. Because this vector lies in the basal plane, no plastic strain parallel to the c-axis is present. However, such a strain can be produced by twinning; the easiest and most common is $\{10\bar{1}2\}$ (Tenckhoff, 1968). Also, a prismatic slip $\{10\bar{1}0\}(11\bar{2}0)$ and a pyramidal slip $\{10\bar{1}1\}(11\bar{2}0)$ were observed, but their critical resolved shear stress at room temperature was one hundred-times greater than that for basal plane (Kelley & Hosford, 1968). This can be not sufficient to accommodate an arbitrary change in the shape as it is in the case of copper or aluminium which possess at least 12 independent slip systems.

Polycrystalline magnesium samples of purity 99.9 % were annealed at a temperature of 400 °C during 3 hr in the flow of N₂ gas. This ensures that initially the samples contain only residual defects which do not affect the positron characteristics. The measurement of the positron lifetime spectra for such virgin samples revealed only one lifetime component equal to 226±1 ps. As it was reported, this value corresponds to the bulk value for magnesium.

The surface of such a sample was sliding in a tribotester against a rotated disc made from the martensitic steel (steel SW18 hardness about 670 HV0.1) of diameter 50 mm with a certain load. The treatment was performed in air, no oxidation was observed. The velocity of the disc relative to the surface of the sample was equal to 5 cm/s. During this test we obtained the value of the friction coefficient equal to 0.24 and the specific wear rate, defined as worn volume per unit sliding distance per unit load, equal to $(8.0 \pm 0.8) \times 10^{-13} \text{ m}^3/\text{N m}$.

The measurements of the positron lifetime spectra in the sequenced procedure reveal only one lifetime component. This was a surprise, because usually in deformed metals or alloys, due to the existence of several kinds of defects, two or three components are observed. The values of the positron lifetime ranged from about 248 ps to the bulk value equal to 226 ps. The former value is slightly lower than the value of the lifetime for the positron trapped in the single vacancy in magnesium host, i.e. 253 ps (Schaefer, 1987). Thus the detected values did not originate from this defect. We can argue that this is due to dislocations decorated by vacancies, or jogs. Such defects located near a dislocation are deformed due to a stress field, and the positron lifetime becomes lower than that in the single vacancy. It can be concluded by analogy to other metals, i.e., aluminium (Häkkinen et al., 1989), nickel and iron (Onitsuka et al., 2001) and zinc (Campillo et al., 2000) because no theoretical data reported yet. The net dislocation line is a weak trap for positrons, but it is accompanied by jogs, vacancies or interstitial atoms produced during its motion caused by plastic deformation. The positrons annihilating in all of those defects and in the bulk contribute to the lifetime spectrum but due to the finite time resolution of the spectrometer one can resolve only the average value. Thus, the positron lifetime obtained from the deconvolution procedure may be treated as the mean lifetime.

Fig. 4 presents the dependency of the measured positron lifetime depth profile for four values of the applied load during the sliding treatment of the magnesium samples. The samples were exposed to the friction treatment at the distance of 9 m in all cases. A common feature of the dependencies is a gradual decrease of the positron lifetime with depth down to the bulk value at a certain depth. It tags the total range of the SZ, which depends on the applied load. For the lower value of the load, 25 N, it is about 150 µm, and for the highest, 150 N, it is 440 µm (see Table 1). As in our former studies concerning the SZ in pure aluminium the experimental dependencies can be well described by a simple exponential decay function (Dryzek & Dryzek 2004),

$$\tau(z) = \tau_0 + a \exp(-z / d_0), \quad (1)$$

where z is the depth or the thickness of the material etched away τ_0 , a and d_0 are the fitted parameters. The solid line in Fig.4 presents the best fit of relation (1) to the experimental points obtained for the highest applied load of 150 N. The fitted parameters obtained for all samples are gathered in Table 1. The parameter d_0 characterizes the SZ. It is worth noticing that its value increases when the load increases (Table 1).

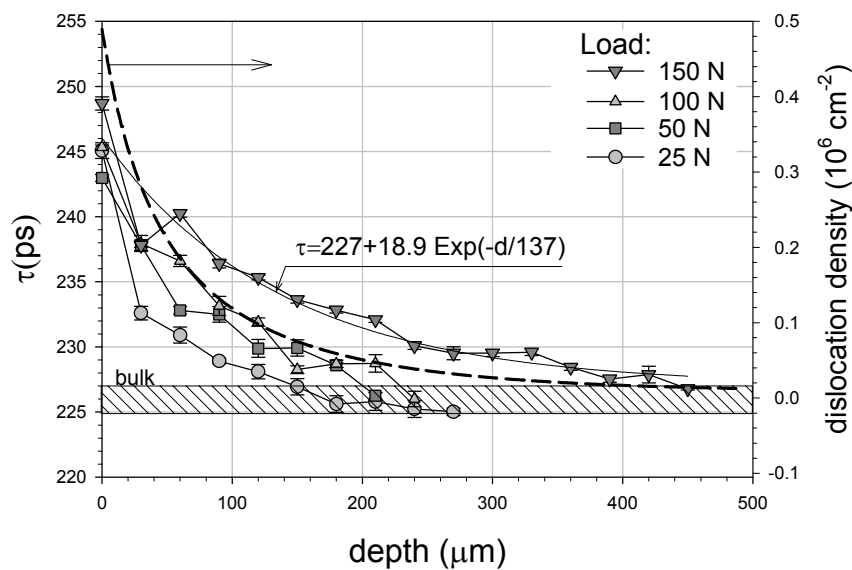


Fig. 4. Depth profile of the positron lifetime measured for pure magnesium samples after sliding against a rotated martensitic steel disc during 3 min (sliding distance 9 m) with different applied loads. The solid line presents the best fit of relation (1) to the experimental points obtained for the load of 150 N. The dashed line corresponds to the estimated dislocation density depth profile (load 150 N) obtained from relation (2) taking into account relation (1). The shaded region represents the bulk positron lifetime in pure magnesium (Dryzek et al., 2005).

Surface Treatment		τ_0 (ps)	a (ps)	d_0 (μm)	Total range of the SZ (μm)
Load (N)	Sliding distance (m)				
25	9	225.9±0.6	18.5±1.3	40±6	150±30
50	9	226.2±1.5	16.6±1.5	82±20	200±30
100	9	225.3±1.7	19.4±1.7	98±23	240±30
150	9	227.0±1.8	19.0±1.4	137±28	440±30
25	45	230.1±1.0	18.4±1.3	50.8±9.0	>270 ±30

Table 1. Values of the parameters from relation (1) fitted to the experimental points presented in Figs 4 and 5 obtained for well annealed magnesium samples after dry sliding against martensitic steel; the sliding conditions are stated in the first column.

If we treat the measured positron lifetime as the mean positron lifetime and assume that dislocations are the traps localizing positrons, dislocation density can be estimated. According to the trapping model, the mean positron lifetime is related to the dislocation density, ρ_d , as follows:

$$\bar{\tau} = \tau_{bulk} \frac{1 + \tau_{sat} \nu \rho_d / b}{1 + \tau_{bulk} \nu \rho_d / b}, \tag{2}$$

where τ_{bulk} =226 ps and τ_{sat} is the lifetime for a dislocation saturated sample; in our case we assume it is equal to 248 ps. Further, b is the Burgers vector and ν is the trapping efficiency;

in the case of a dislocation in magnesium it is equal to $3.23 \times 10^{-6} \text{ s}^{-1} \text{ cm}^3$ (Mehta et al., 2004). Putting relation (1) into relation (2) as the mean positron lifetime, we can estimate the dislocation density profile. In Fig. 4 the dashed line follows such a profile for a sample exposed to sliding with a load of 150 N. It indicates a strong gradient of the dislocation concentration in the SZ. This gradient slightly decreases with the increase of the sliding distance but the value of the positron lifetime at the worn surface does not change, as it is visible in Fig. 5. In this figure the positron lifetime profiles obtained for two samples exposed to the sliding treatment with the same load of 100 N but for different sliding distances are depicted.

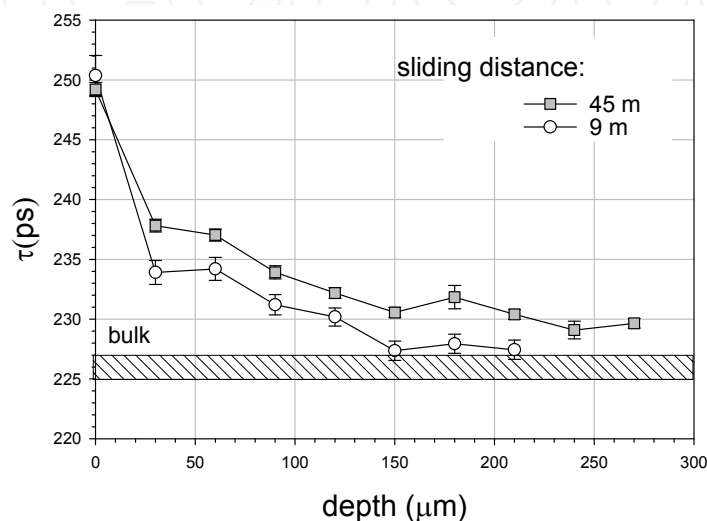


Fig. 5. Depth profile of the positron lifetime measured for the pure magnesium samples exposed to the dry sliding against a martensitic steel disc with a load of 25 N at the sliding distances 9 m and 45 m, respectively. The shaded region represents the bulk positron lifetime in pure magnesium (Dryzek et al., 2005)

4.2 Microhardness profile in the SZ

The microhardness profiles measured using the commercially available Micro-Combi-Tester (CSEM) for the samples after sliding with different loads exhibit different shapes. In this measurement the Vickers indenter with the maximum load of 20 mN was applied. The velocity of the load increase was equal to 40 mN/min. The profile is depicted in the Fig. 6 for two selected samples. It is interesting to notice that the microhardness initially increases with the depth from the worn surface and at a certain depth reaches the maximum and then decays to the bulk value. The total depth of the microhardness profile is about 120 μm, which is lower than that detected by the positron technique (see Table 1). We have also observed a similar fact for the aluminium alloys (Dryzek & Dryzek, 2006). The discrepancy between the microhardness profile and positron lifetime profile can be explained by the fact that only positron technique is sensitive to point defects created in a great amount during plastic deformation while the microhardness is not.

4.3 The SZ in pure magnesium detected by slow positron beam

The conventional techniques where positrons are emitted from the radioactive source, i.e. ^{22}Na are not suitable to detect the region close to the worn surface. The convenient tool for this purpose is the positron beam technique where monoenergetic positrons forming a beam

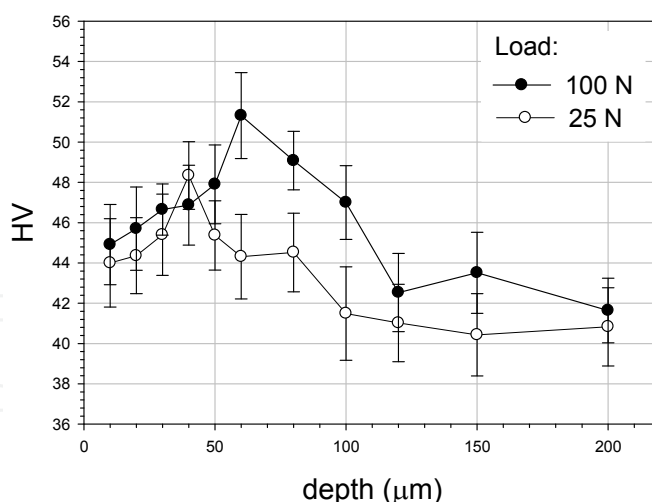


Fig. 6. Depth profiles of the microhardness measured for pure magnesium samples after dry sliding against a rotated martensitic steel disc during 3 min (sliding distance 9 m) with different applied loads (Dryzek et al., 2005)

are implanted in the sample at a desired depth. In our experiment the positron energy was ranged from 0.1 keV to 25 keV. This allows us to scan a magnesium sample to the depth up to 4 μm from the top surface, which previously was exposed to dry sliding. In this case the so called S-parameter was measured as the function of positron energy instead of positron lifetime. The so-called S-parameter defined as the ratio of the area under the fixed center part of the annihilation line to the area under the whole annihilation line is a suitable line shape parameter that characterizes the annihilation line broadening. If the annihilation with electrons having lower momentum increases, the value of the S-parameter also increases. This takes place when positrons annihilate from the localized state, e.g. trapped in vacancies or vacancy clusters where the electron density is lower in comparison to the interstitial region. Similarly to the positron lifetime, the value of the S-parameter can tag the change in the vacancy or vacancy cluster concentration.

Fig. 7 presents the obtained dependence for the well annealed reference sample and samples whose surfaces were exposed to dry sliding. The value of the S-parameter on the surface is significantly lower than in bulk at the depth of 4 μm. This indicates that on the surface there is present a layer different from the bulk, i.e. the magnesium oxide layer. The change in the slope of the dependencies at the depth of c.a. 100 nm indicates that this is the thickness of the magnesium oxide layer. Using the VEPFIT (Veen et al., 1990) program, we were able to describe the experimental data for the well annealed sample assuming existence of two regions, the first at the surface and second inside. The thickness of the outer layer evaluated from the fit was equal to 107 ± 1 nm and the positron diffusion length was equal to 70 ± 1 nm. This value in the interior equals to 780 ± 150 nm which seems to be extremely large in comparison to other materials. The latter would correspond to the positron diffusion in the polycrystalline bulk magnesium. For the sample whose surface was exposed to sliding with the highest load of 100 N the outer layer thickness increased to 150 ± 10 nm. This is connected with the fact that during sliding the mixed layer containing the magnesium oxide is created on the surface. Its thickness increases with increase of the applied load. The increase of the sliding time does not affect the thickness of the mixed layer as it can be seen in Fig. 8. The etching of the samples in the in a 5% water solution of acetic acid reduced the thickness of the oxide layer but did not remove it.

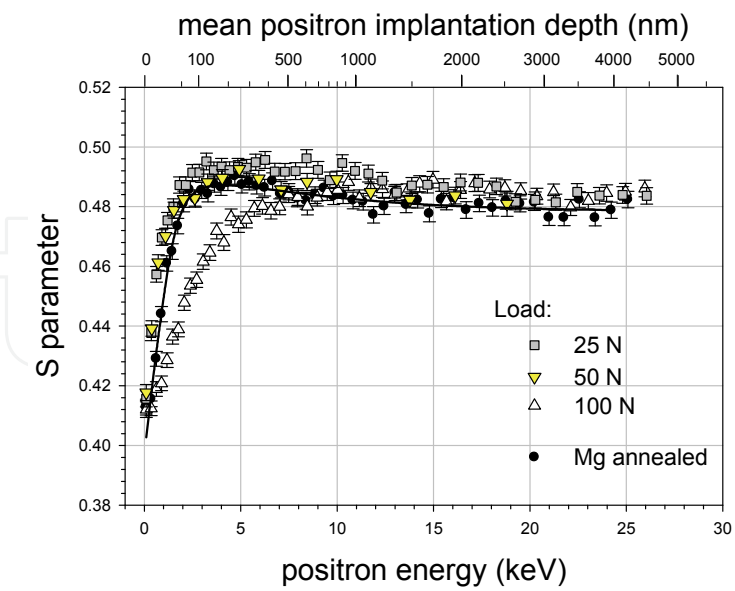


Fig. 7. The S-parameter vs. positron beam energy for the reference sample and samples after dry sliding with different loads for the sliding distance of 9 m. The solid line represents the theoretical dependence obtained using VEPFIT program for the well annealed magnesium sample (Dryzek et al., 2007).

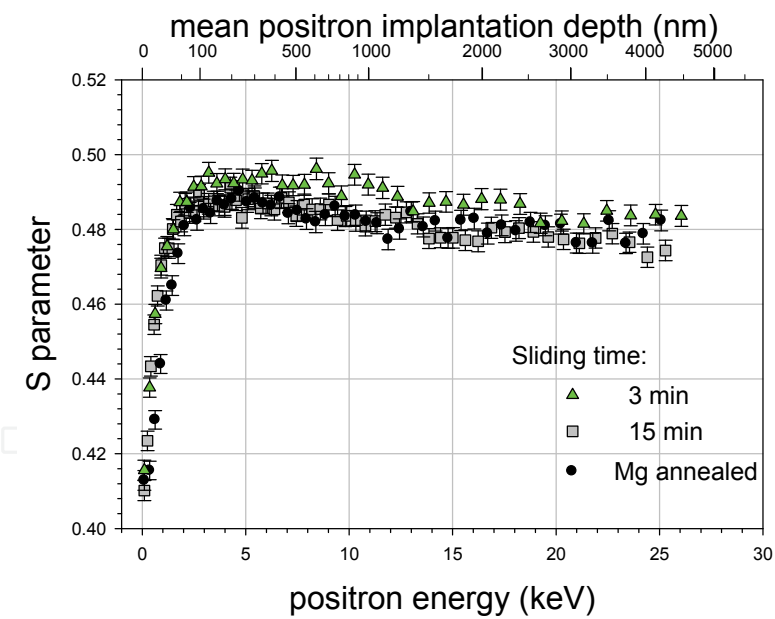


Fig. 8. The S-parameter vs. positron beam energy for reference sample and samples after dry sliding for different sliding times corresponding to sliding distances 9 m and 45 m for the load of 25 N (Dryzek et al., 2007).

Concluding, it can be stated that on and under the worn surface in pure magnesium after dry sliding mainly dislocations with accompanying defects, like vacancies and jogs, are created. Their concentration decays exponentially with increase of depth. The total range of the SZ is more than one hundred micrometers and depends on the applied load and sliding distance. Thus the type of the crystal structure and lack of the well developed slip systems

has minor effect on the total range of the SZ in magnesium. The mixed layer containing the magnesium oxide created on the worn surface has the thickness of about 150 nm.

5. The SZ in magnesium alloy AZ31

In technical applications the pure magnesium is not in use then we performed similar studies for magnesium-based alloy Mg96Al3Zn1 (Goodfellow), temper as drawn, analogous to the commercial AZ31 alloy. The Mg-Al-Zn alloy system is well known. The addition of Al, Zn or both these elements results in increase in the strength and decrease in the ductility of the magnesium alloy. Al and Zn both act as solid solution strengtheners. Both alloying elements form precipitates with Mg in alloy matrix, e.g. $Mg_{17}Al_{12}$ discontinuous intermetallic phase (Bowles et al., 2007). However, XRD measurements did not reveal the existence of such a phase in our sample.

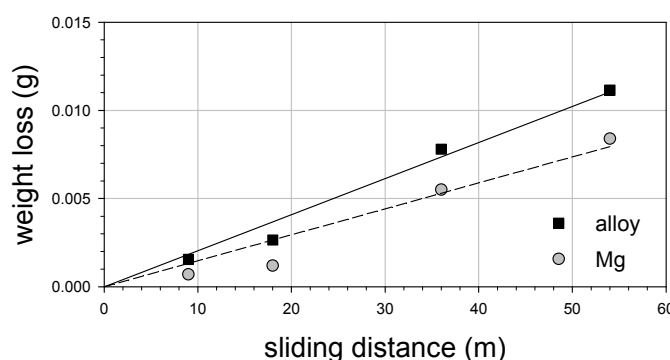


Fig. 9. Weight loss of the magnesium alloy and pure magnesium pins as functions of sliding distance against the rotated steel disk at the velocity of 5 cm/s and the applied load of 100 N (Dryzek & Dryzek 2007).

We compared the specific wear rates calculated from the weight loss measured for different sliding distances for the alloy and pure magnesium (99.9% purity) in Fig. 9. The specific wear rate for the alloy is equal to $(1.11 \pm 0.10) \times 10^{-12} \text{ m}^3/\text{Nm}$ and is about 40% higher than for pure magnesium. The measured values of the friction coefficient of the alloy and magnesium against the steel disc, equal to 0.20 and 0.24, respectively, are comparable.

The measurement of the positron lifetime spectrum for the virgin, reference sample of the alloy reveals only one lifetime component equal to $226 \pm 1 \text{ ps}$. This value is the same as the value of positron lifetime in bulk in pure magnesium and will be treated as the bulk lifetime in the alloy. After dry sliding, similarly to pure magnesium in all measured lifetime spectra only one lifetime component was resolved. Its value ranged from the bulk value, equal to $226 \pm 1 \text{ ps}$, to about 240 ps. Nevertheless, on closer inspection a second, long-lived component equal c.a. 1450 ps was found but its intensity was close to 1 %.

The sequenced measurement of the positron lifetime spectrum after etching away a certain thickness of the alloy samples after sliding at the same distance of 36 m with different loads applied: 50 N, 100 N and 150 N reveals well defined depth profiles. In Fig. 10, the value of the main lifetime component and the intensity of the long-lived component are depicted as functions of depth. The striking feature of the results obtained is the short range of the SZ, which is additionally hardly affected by the applied load. The total range is about 100 μm and it is much lower than in pure magnesium. (For comparison the depth profile of the positron lifetime measured for pure magnesium after sliding in similar conditions is

presented in this figure as well.) As above the equation (1) describes well the decay of the positron lifetime as the function of depth.

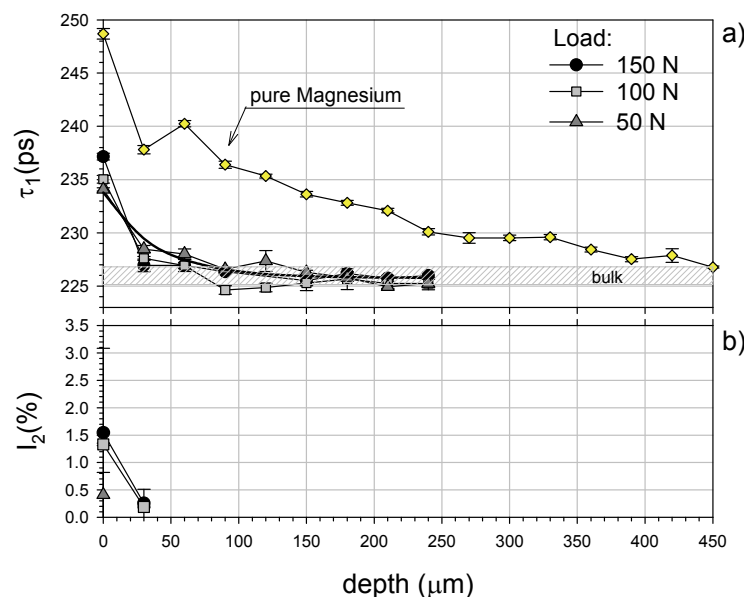


Fig. 10. The main positron lifetime a) and the intensity of the long-lived component b) as functions of depth or etched layer thickness measured for the alloy samples after sliding at the same distance of 36 m with different loads applied: 50 N, 100 N and 150 N. For comparison, the value of the main positron lifetime component for the pure magnesium sample which was exposed to sliding with the normal load of 150 N at a sliding distance of 9 m is also presented a). The solid line represents the best fit of equation (1) to the experimental points measured for the alloy sample exposed to sliding with the normal load of 100 N. The reference bulk positron lifetime in the alloy is also indicated (hatched area) (Dryzek & Dryzek 2007).

It is interesting that in opposition to the results for pure magnesium the d_0 parameter decreases with the increase of the applied load – for the load of 50 N it is equal to $38.0 \pm 1 \mu\text{m}$ for the load of 100 N it is equal to $23.0 \pm 4 \mu\text{m}$ and for 150 N it is equal to $12.6 \pm 3 \mu\text{m}$. The solid line in Fig. 10 a represents an example of the best fit of the equation (1) to the experimental points. The intensity of the long-lived component, Fig. 10 b, decays quickly and at the depth of about 30 μm disappears.

In Fig. 11 a, we depicted the profiles of the main lifetime component for the alloy samples after sliding with the same load of 100 N for three different sliding distances. The exponential decay of the τ_1 value with depth is clearly visible and the total depth of the SZ is about 50 μm. The d_0 parameter in all cases is about $15 \pm 2 \mu\text{m}$ and does not depend on sliding distance within the accuracy of the measurement. In Fig. 11 b, the decay of the intensity of the long-lived component is clearly visible and at the depth of about 30 μm it also disappears.

The Vickers microhardness profile was measured for two selected samples whose surfaces were exposed to sliding. The obtained results are depicted in Fig. 12. The microhardness value decreases quickly with depth and the dependency can be described by an exponential decay function, similar to that given by equation (1). The best fit is presented as the solid line in Fig. 12. The value of the parameter d_0 was equal to $26.2 \pm 7 \mu\text{m}$ for the sample exposed

to sliding with the applied load of 100 N and the sliding distance of 54 m and $16.2 \pm 2 \mu\text{m}$ for another sample with the applied load of 50 N and the sliding distance of 18 m. These values correspond well with those obtained from the positron lifetime measurement (Fig. 10a, 11a) and they confirm the short range of the SZ created in the alloy.

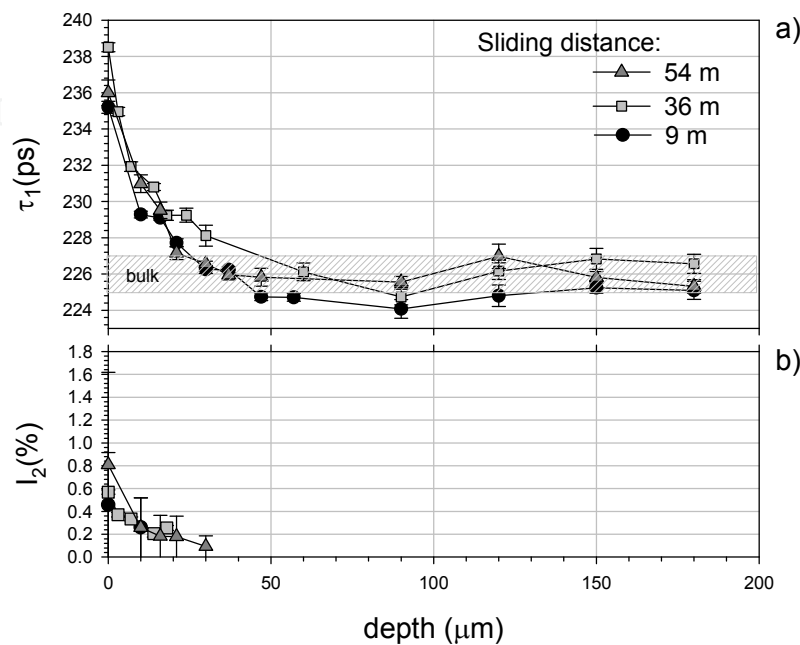


Fig. 11. The main positron lifetime a) and the intensity of the long-lived component b) as functions of depth or etched layer thickness measured for the alloy sample after sliding at different distances with the normal load of 100 N. The reference bulk positron lifetime in the alloy is also indicated (hatched area) (Dryzek & Dryzek 2007).

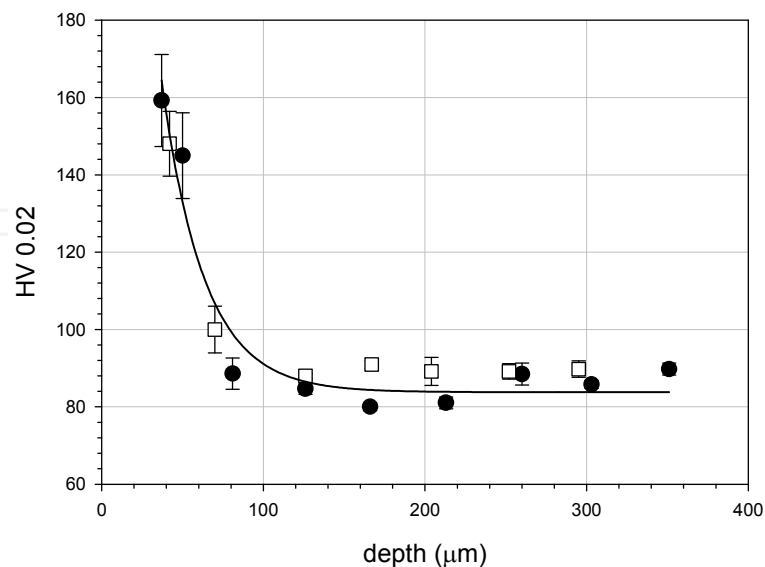


Fig. 12. The Vickers microhardness profile for the alloy samples after sliding at the distance of 18 m with the normal load of 50 N (open square) and at the distance of 54 m with normal load of 100 N (filled circles). The solid line (a) is the best fit of the exponential function $HV = 89.4 + 779 \exp(-d[\mu\text{m}]/16.2)$ to the open square points (Dryzek & Dryzek 2007).

The short range of the SZ in the alloy in comparison to the pure magnesium indicates the great role of alloying in the process of its creation. Adding other atoms into this structure we can effectively obstruct the slip system, thus a depth expansion of deformation induced on the worn surface is hindered. A similar phenomenon was observed in aluminium alloys for which the range of the SZ was shortened in comparison to pure aluminium (Dryzek & Dryzek, 2004). This supports the role of dislocations in forming of the SZ which originated on or just below the worn surface and can move into the interior of the damaged sample. Adding atoms, precipitates or other structural elements which inhibit movement of dislocations in the alloy host influences also the depth expansion of the SZ. As we have found, the total range of the SZ reflects the range of the plastic deformation. It is worth noticing that the range of the SZ correlates inversely with the wear rate. Above we marked that for the alloy the wear rate is higher than for pure magnesium. Similar correlations were observed also for aluminium alloys. During sliding energy dissipates causing creation of structural defects, vacancies, dislocations and others. The short range of the SZ implies that this energy is deposited in a narrow region near the surface. Thus one could expect more defects there than would be in a wider range. If structural defects are responsible for wear thus more defects should imply higher wear rate. Our experimental observations are focused rather on the microscopic origin of the wear induced by crystalline defects. Nevertheless, their distribution and total depth of plastic deformation underneath the worn surface is the macroscopic parameter, which is omitted in other wear models.

The detection of the lifetime component equal to c.a. 1450 ± 100 ps in the measured spectra is a surprise. Such a weak long-lived component between 1000 and 5000 ps was reported in nanocrystalline metals like iron, nickel and was attributed to the formation of ortho-positronium at the surface of voids. Positronium is the positron-electron bound state similar to hydrogen and can be created for instance in molecular solids, where the empty volume allows to create it. The minimal radius of such a volume which is suitable for creation of such a bound state is about 0.19 nm. We believe that voids of radius bigger than this can be located in the SZ at the depth less than 30 μm . More detail calculation allows us to estimate their radius 0.23 ± 0.01 nm. It is quite possible that the voids can be produced on special dislocation arrangements created during plastic deformation at large strains. They could nucleate cracks. It is not excluded that presence of oxide in the surface layer favors formation of positronium.

Concluding the result obtained for alloy AZ31 we can state that the total range of the SZ detected is about 100 μm and it is much lower than that detected for the pure magnesium which was between 150 μm and 440 μm . This can affect the wear process on the surface. The specific wear rate for this alloy has a higher value than for pure magnesium. Thus the alloying of magnesium has the significant role for the SZ constitution.

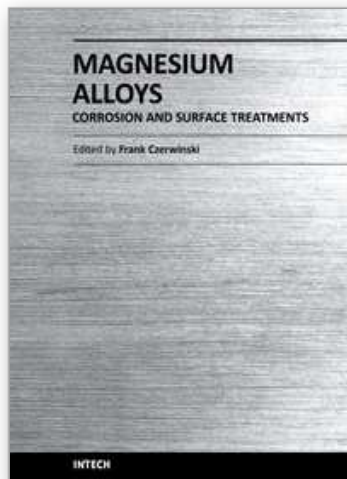
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Magnesium Alloys - Corrosion and Surface Treatments

Edited by Frank Czerwinski

ISBN 978-953-307-972-1

Hard cover, 344 pages

Publisher InTech

Published online 14, January, 2011

Published in print edition January, 2011

A resistance of magnesium alloys to surface degradation is paramount for their applications in automotive, aerospace, consumer electronics and general-purpose markets. An emphasis of this book is on oxidation, corrosion and surface modifications, designed to enhance the alloy surface stability. It covers a nature of oxides grown at elevated temperatures and oxidation characteristics of selected alloys along with elements of general and electrochemical corrosion. Medical applications are considered that explore bio-compatibility of magnesium alloys. Also techniques of surface modifications, designed to improve not only corrosion resistance but also corrosion fatigue, wear and other behaviors, are described. The book represents a valuable resource for scientists and engineers from academia and industry.

How to reference

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Ewa Dryzek and Jerzy Dryzek (2011). Application of Positron Annihilation Spectroscopy to Studies of Subsurface Zones Induced by Wear in Magnesium and Its Alloy AZ31, Magnesium Alloys - Corrosion and Surface Treatments, Frank Czerwinski (Ed.), ISBN: 978-953-307-972-1, InTech, Available from: <http://www.intechopen.com/books/magnesium-alloys-corrosion-and-surface-treatments/application-of-positron-annihilation-spectroscopy-to-studies-of-subsurface-zones-induced-by-wear-in->

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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