Effect of magnetic field on the corrosion of iron as studied by positron annihilation

Ryszard Pietrzak,
Roman Szatanik

Abstract. Lifetime spectra of positron annihilation in iron corroded in a water solution of HCl and in vapour above its surface have been investigated with emphasis on the effect of corrosion time and environment (solution or vapour) as well as of the presence and orientation of the magnetic field on the measured positron annihilation parameters. All the registered positron lifetime spectra consist of two components. For corroded samples, the intensities of the two components as well as the corresponding values of the mean positron lifetime, differ from those for uncorroded material. The corrosion-induced changes in the positron annihilation parameters depend on the corrosion environment (solution or vapour) and on the presence and direction of external magnetic field.

Key words: corrosion • magnetic field • positron annihilation

R. Pietrzak, R. Szatanik✉
Institute of Physics,
Opole University,
48 Oleska Str., 45-052 Opole, Poland,
Tel.: +48 77 452 7250, Fax: +48 77 452 7290,
E-mail: szata@uni.opole.pl

Introduction

It is well known that the early stage of corrosion is related to the crystal lattice defects present in the surface layer of metals. The physical, chemical and metallographical methods commonly used in the studies of corrosion processes are, as a rule, sensitive to the relatively large (in an atomic scale) defects. Therefore, the application of positron annihilation techniques and especially of the positron lifetime spectroscopy, may be the source of very interesting information on the processes occurring in the early stage of corrosion.

The results of many previous investigations [8–12] demonstrated that the corrosion-induced changes in the parameters of the lifetime spectra of positrons annihilating in iron, nickel, and steel depend on the corrosion time and environment, as well as on the state of the surface of corroding metal. After removing the corroded layer several micrometers thick, the positron annihilation parameters achieve the same values as before corrosion.

For many years, the positron annihilation phenomenon is successfully used in investigations of the defect structure of solids. The positron annihilation techniques are especially useful in investigations of the formation and kinetics of small (in an atomic scale) defects, like vacancies, vacancy clusters, dislocations, etc. [4].

The [22]Na positron sources, commonly used in such investigations, emit positrons of a continuous energy

spectrum with a maximum energy value of 0.545 MeV. The positrons can penetrate the surface layers of metals up to the depth of $20 \div 30\ \mu m$. At such depth, the corrosion-induced defects in metals starts to be formed, too. Due to the continuous character of their energy spectrum, the positrons can annihilate already at a depth of a few lattice constants under the surface of corroding metals, and their lifetimes depend on the dimensions and configuration of the defects present in this area [13].

The effect of magnetic field on the kinetics of corrosion has been investigated, however, the results were not unambiguous [1–3]. One the hand, it was affirmed and among others, demonstrated that corrosion of iron and copper in HNO_3 can be distinctly lowered, and even stopped by constant magnetic field though, on the other hand, the magnetic field can also accelerate the corrosion processes, e.g. for titanium [6]. A strong effect occurs of the magnetic field on the growth kinetics of corrosion pits on ferromagnetic steel electrodes, the effect being absent in the case of austenitic steels. Nevertheless, the mechanism of the effect of magnetic field on the rate of corrosion processes remains to be not fully understood.

Earlier theoretical investigations [7] concerned the influence of magnetic field on the kinetics of corrosion, and in particular: flow of the stream of corrosive solution, interaction of the electrolyte with magnetized surface, effect of magnetic field on the moving ions (Lorentz force), effect of the gradient of magnetic field on moving ions, changes in the chemical potential of electrodes due to the action of magnetic field, effect of magnetic field on the concentration of ions and the surface of magnetized electrode.

In the present paper we present the results of experimental investigations of the lifetime spectra of positrons annihilating in iron submitted to corrosion in a water solution of HCl and in the vapour above its surface, in the presence of external magnetic field perpendicular and parallel to the sample surface.

Sample preparation

The iron (99.9%) samples with dimensions of $10 \times 10 \times 1\ mm^3$ were used. After cleaning in ethanol and in a derusting solution (Fosol) the samples were tempered for 1 h in vacuum ($p < 10^{-3}$ mbar) at 850°C and slowly (1 K/min) cooled to room temperature. After such heat-treatment, the lifetime spectra of positron annihilating in investigated materials were determined using a conventional fast-slow type spectrometer of 206 ps resolution.

Next, the samples were submitted to corrosion in a 3% water solution of HCl or in the vapour above its surface. Corrosion was carried at room temperature in the presence of constant magnetic field ($B = 276$ mT), or in the absence of magnetic field. The arrangement shown in Fig. 1 enabled to corrode 4 samples (2 in solution and 2 in vapour) in two different orientations of their surfaces with respect to the magnetic field.

After defined corrosion time, the samples were rinsed in ethanol and degassed in vacuum, and then positron lifetime spectra were determined again.
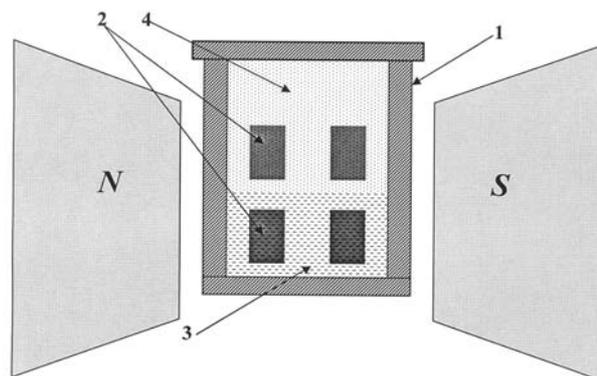

Fig. 1. Scheme of the apparatus used to investigate corrosion in HCl solution and in vapours above its surface in the presence of magnetic field: 1 – plexiglass vessel; 2 – iron samples; 3 – water solution of HCl; 4 – HCl vapour.

Determination and analysis of positron lifetime spectra

The ^{22}Na positron source was placed between two samples corroded under the same conditions. The registered positron lifetime spectra were analysed using the Lifetime (LT) program [5]. Decomposition of each of the spectra into 1, 2 and 3 components has been proved by the χ^2 test. It has been found that in all the cases the decomposition into two components assures the best fit to the experimental data. The existence of these two components, with different lifetimes τ_1 and τ_2, and the two corresponding intensities I_1 and I_2, may be interpreted assuming that the positrons annihilate from the free state between the lattice sites (lifetime τ_f) and being trapped in defects of one or more types (lifetime τ_{D_i}, $i = 1,2,3\ldots$).

In many cases, however, the spectrometer resolution is insufficient for separation of all the components of analysed spectrum. In such situations one of the component obtained by analysis of the registered spectrum is a result of the overlapping of two real components with similar lifetimes.

A comparison of the values of positron lifetimes obtained in the present study with the literature data in pure iron, devoid of large-size defects, suggests that in our case the component with shorter $\tau_{1,exp}$ is probably, in fact, a sum of two components connected with annihilation in the free state (τ_f) and in defects of small dimensions (τ_{D_1}) – vacancies and dislocations, further called defects of I-type. The component with a longer lifetime $\tau_{2,exp}$ corresponds to the annihilation in defects of large sizes (e.g. multivacancy clusters, voids, grain and phase boundaries, etc.) further referred to as the II-type defects.

The aim of the present communication is the presentation of the possibility of application of the positron lifetime method in investigations of the formation and growth of the corrosion pits and the effect of magnetic field on these processes. Therefore, only the data on the changes in the parameters of the long-living component of the positron annihilation spectrum ($\tau_{2,exp}$ and $I_{2,exp}$) will be presented and analysed. The changes in the intensity $I_{2,exp}$ can be ascribed to the changes in the annihilation rate in large size defects of the II-type, what, in first approximation, corresponds to the changes in concen-

tration of these defects. Treating these defects as the multivacancy clusters one should assume, in accordance with [13], that the value of mean positron lifetime $\tau_{2,exp}$ depends on the number of the vacancies in a cluster.

Results of measurements and their interpretation

Effect of corrosion time

First, the effect of corrosion time on the positron lifetime spectra has been investigated for iron samples corroded in a 3% water solution of HCl and in the vapour above its surface, in the absence of external magnetic field ($B = 0$). The obtained values of $\tau_{1,exp}$ are weighted averages of at least two lifetimes with similar values, steming from annihilation in the free state and in the neighbourhood of the edge dislocations (117÷150 ps) [4]. Measured values of $\tau_{2,exp}$, ranging from 280 to 340 ps (Fig. 2) correspond, most probably, to the annihilation of positrons in the corrosion pits in the form of clusters consisting of 5÷10 vacancies, located at the grain boundaries. As it is seen in Fig. 2, the greatest changes in the $\tau_{2,exp}$ and $I_{2,exp}$ parameters occur in the early stage of corrosion (up to 20 h). The changes in the value of $\tau_{2,exp}$ for the samples corroded in solution are greater than those for the samples corroded in vapour. Probably, the sizes of the corrosion pits forming at the grain boundaries during the corrosion in solution are greater than those forming during the corrosion in vapour. Increase in the size of the corrosion pits occurs at the cost of their concentration, probably due to the joining of the neighbouring pits.

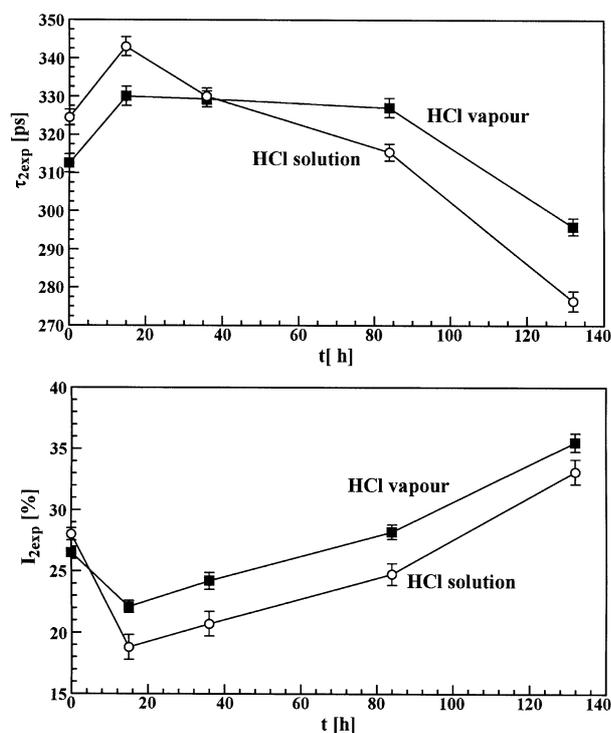The next 70 h corrosion in vapour does not change the $\tau_{2,exp}$ value, but after this period $\tau_{2,exp}$ systematically decreases with increasing corrosion time. In contrast to that, for samples corroded in solution a systematic decrease in the $\tau_{2,exp}$ value, accompanied by an increase of $I_{2,exp}$, is observed for corrosion times greater than 20 h. The data presented in Fig. 2 permit to state that after corrosion lasting longer that 40 h, both the dimensions and concentrations of pits formed in samples corroding in solution are smaller than those for samples corroding in vapour.

Effect of magnetic field

As already mentioned in the introductory part of the present paper, the effect of magnetic field on the chemical processes is occurring during the corrosion. Eventual changes in the kinetics of these processes may lead to changes in the defect structure of the corroded surface layer.

Figure 3 presents the relative changes in the values of the $\tau_{2,exp}$ and $I_{2,exp}$ parameters due to the 80 h corrosion in three situations:
a) corrosion in the absence of external magnetic field ($B = 0$),
b) corrosion in the magnetic field perpendicular to the corroding surface ($\otimes$),
c) corrosion in the magnetic field parallel to the corroding surface ($\parallel$).

Value of the $\tau_{2,exp}$ parameter for samples corroded in HCl vapour is greater than for non-corrodible samples. An opposite effect is observed for the samples corroded in the HCl solution. The external magnetic field enhances the changes in the $\tau_{2,exp}$ value for samples corroding in the HCl vapour. The enhancing effect of the field parallel to the corroding surface is stronger than that of the perpendicular field. For samples corroding in HCl solution, the presence of external magnetic field
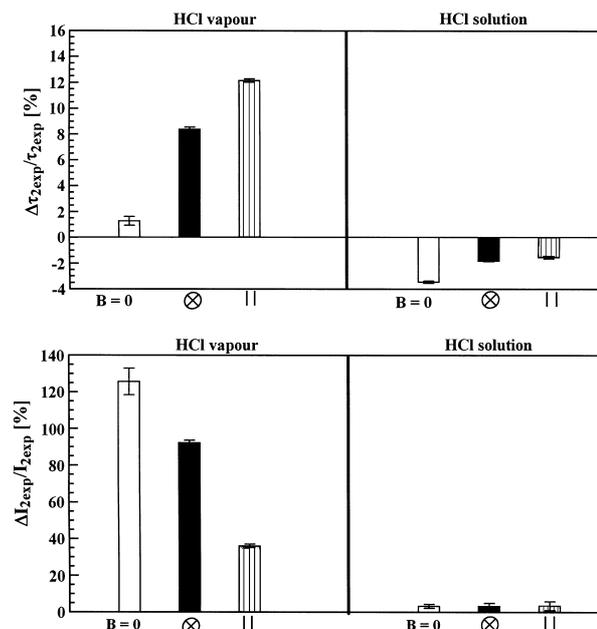

Fig. 2. Dependences of the $\tau_{2,exp}$ and $I_{2,exp}$ parameters for iron corroded in a 3% water solution of HCl and in its vapours on the corrosion time.

Fig. 3. Relative changes in the $\tau_{2,exp}$ and $I_{2,exp}$ parameters for iron after corrosion in a water solution of HCl and in HCl vapour in the absence of magnetic field ($B = 0$), and in the magnetic field perpendicular ($\otimes$) and parallel ($\parallel$) to the corroding surface.

causes a decrease in the value of $\tau_{2,exp}$ with respect to the non-corrodible sample, and the relative decrease of the $\tau_{2,exp}$ value does not depend on the direction of magnetic field.

The intensity $I_{2,exp}$ for the samples corroded in the HCl vapour is distinctly greater than that before corrosion, whereas for the samples corroded in solution it is practically the same as before corrosion. The external magnetic field retards the changes in the intensity $I_{2,exp}$ of this component for the samples corroding in vapour, and the retardation effect of the field parallel to the surface of corroding sample is weaker than that of the perpendicular field.

Assuming that the observed changes in the mean lifetime value $\tau_{2,exp}$ and in the intensity $I_{2,exp}$ are connected with the concentration and dimensions of the corrosion-induced defects, the results presented in Fig. 3 can be interpreted as follows. During the corrosion in the HCl solution, large size defects (multivacancy corrosion pits) are formed or the domain boundaries are enlarged. The external magnetic field retards these processes, the retardation effect in magnetic field parallel to the corroding surface being stronger than that in the perpendicular field. The difference in the relative changes in the $\tau_{2,exp}$ and $I_{2,exp}$ values for samples corroding in solution with respect to those for samples corroding in vapour results from the difference in mobility of Cl^- ions and concentration of oxygen – in solution both of them being smaller than in vapour.

Conclusions

The results of the present study may be summarized as follows:

1. The intensity $I_{2,exp}$ and the mean positron lifetime $\tau_{2,exp}$ of the long-living component of positron lifetime spectra depend on the time and physicochemical conditions of corrosion of iron.
2. External magnetic fields distinctly affect the defect structure of the corroded near-surface layers of the investigated samples.
3. Magnetic field changes the probability of the two-quanta annihilation of positrons in the subsurface defects in the investigated materials.
4. Corrosion-induced changes in the $I_{2,exp}$ and $\tau_{2,exp}$ values for the samples corroded in HCl vapours are distinctly greater than those for the samples corroding in a water solution of HCl.

5. The directions of changes in the positron annihilation parameters for iron corroded in the presence of external magnetic field in HCl vapours and in a HCl solution are of opposite signs.

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