Proceedings of the 41st Polish Seminar on Positron Annihilation, Lublin, September 9–13, 2013

The Influence of a Magnetic Field on the Formation of Corrosion Defects in Selected Metals and Steels, Analysed Using Positron Annihilation Method

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The method of positron lifetime measurement was used to analyse the influence of a magnetic field on the kinetics of corrosion defect formation in near-surface layers of iron, titanium as well as S20 and S0H18N9 steel grades. The listed metals, which belong to ferro- and paramagnetic materials, have different sensitivity to corrosion. It was found that not only the presence of a magnetic field, but also its direction influence the dimensions and the concentration of defects formed during corrosion.

DOI: 10.12693/APhysPolA.125.733
PACS: 78.70.Bj, 61.72.Cc, 82.45.Bb

1. Introduction

Corrosion is a physical and chemical phenomenon always connected with the formation and movement of defects in near-surface layers of the corroding material. The last dozen of years has also seen the use of methods known from nuclear physics, particularly those based on positron annihilation. Publications [1–9] demonstrate that measurements of positron lifetimes in metals with corroded surfaces provide valuable information about early stages of corrosion defect formation, whose stages usually cannot be studied using other physical or chemical methods. Positrons emitted from β^r radioactive sources (e.g., ^{22}Na) with a continuous energy spectrum penetrate the near-surface areas of metals down to the depth of several dozen micrometres (e.g., down to the depth of 41 μm in Ti and 29 μm in iron [10]). In order to develop effective methods of preventing corrosion, one must fully understand the impact of various external factors on this phenomenon, such as a magnetic field. The results of experimental research are also ambiguous in this regard. In some metals (e.g., iron and copper), a magnetic field inhibits corrosion in some conditions, but in other metals (Ti), the field accelerates it. Kelly [11] found that an external magnetic field accelerates corrosion processes in ferromagnetic iron and steel, but has no visible impact on corrosion in austenitic steel. Linhardt and co-workers [12] demonstrated that as long as the metal is passive, the magnetic field has no impact on the kinetics of corrosion pit formation in AISI 304 austenitic steel. In publications [8, 9], we have demonstrated that the changes in the intensity of the defect component of positron lifetime spectra for iron and S20 steel are clearly smaller if the samples were "aged" in an external magnetic field before corroding. This can be due to the following changes:

a) in the energetic structure of magnetic domains, or
b) in the structure of the passive layer on the surface of metal.

From the physical point of view, the passive layer can be treated as a membrane conducting ions and defects, inside which there is a strong electrical field.

2. Preparation of samples for research

Positron annihilation was studied in 99.99% pure Fe and Ti samples, as well as in steel grades of the percentage compositions presented in Table I. The samples were cylindrical with 10 mm in diameter and thickness of 2 mm. In order to eliminate above-equilibrium defects all samples were annealed for 3 h in vacuum ($p < 10^{-3}$ mbar) at temperatures: 850 °C for Fe, 500 °C and 1100 °C for Ti, and 500 °C for both steel grades and slowly cooled at the rate of 1 °C/min to room temperature. Then for the annealed samples positron lifetimes were measured.

TABLE I

Percentage compositions of the investigated steel grades.

	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	V
S20	0.22	–	1.1	–	–	–	–	–	–	–
S0H18N9	0.012	0.29	1.13	0.028	0.026	18.37	8.12	0.36	0.35	0.09

For further annihilation research, samples were prepared as follows: selected samples were magnetically aged, placed between the poles of a magnet for 150 h perpendicular or parallel to the magnetic induction vector. The magnetic field had the induction of $B = 276$ mT. Next, the samples, appropriately oriented relative to the magnetic field, were placed in a plexiglass container above the surface of a 3% water HCl solution, where they corroded for 150 h in the vapour from this solution (Fig. 1). Some samples were subjected to corrosion directly after annealing, without being held in a magnetic field.

Positron lifetime spectra were measured using a Fast–Fast spectrometer with the resolution of 275 ps and spectrum parameters were calculated using the Lifetime 9 computer programme.

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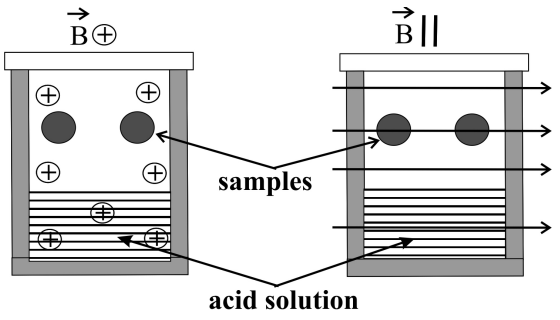

Fig. 1. Orientation of samples in a magnetic field: perpendicular ⊕ or parallel ‖ to the surface of the sample.

3. Results and interpretation

This publication presents the results of analysing positron lifetime in ferro- and paramagnetic metals (Fe, Ti, S20, and S0H18N9 steel grades). Fe and S20 steel are ferromagnetic and susceptible to pit corrosion, while Ti and S0H18N9 steel are paramagnetic and resistant to corrosion.

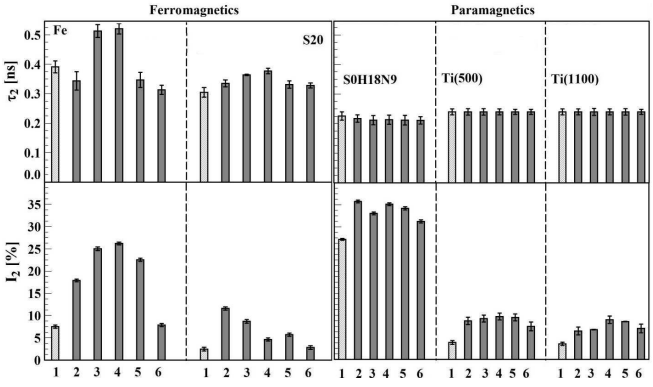

Fig. 2. Diagrams of lifetimes (τ_2) and intensities (I_2) of the second component of positron lifetime spectra in Fe, S20, and S0H18N9 steel grades, as well as Ti before corrosion and after corrosion in a magnetic field (the marking of the samples is to be found in the text).

Figure 2 shows diagrams τ_2 and I_2 of the second component of positron lifetime spectra for samples marked further in the text as follows: (1) before corrosion, (2) corroding outside the magnetic field, directly after annealing, (3) corroding in a perpendicular magnetic field directly after annealing, (4) corroding after "magnetic aging" in a perpendicular magnetic field, (5) corroding in a parallel magnetic field directly after annealing, (6) corroding after "magnetic aging" in a parallel magnetic field, Ti(500) — titanium samples annealed at 500 °C, Ti(1100) — titanium samples annealed at 1100 °C.

Numerical values of τ_2 indicate that in iron and steel positrons annihilate in multi-vacancy clusters, while in titanium in vacancies [13–15]. In all cases, the intensities of this component are clearly greater after corrosion than before it. However, the lifetime of positrons depends on the direction of the external magnetic field in which corrosion occurred. It can be simplistically assumed that in the ferromagnetics for samples (2) the values of τ_2 remain — within the limits of error — unchanged. On the other hand, for samples (3) and (5) these values vary. In titanium (a paramagnetic), magnetic conditions do not influence the values of lifetime τ_2. Relative changes of intensities of this component are greater in ferromagnetic materials than in paramagnetic metals.

Based on the multi-state annihilation model [16], it can be assumed that in the analysed ferromagnetics, after magnetic aging, conditions arise for the creation of above-equilibrium defects which easily form multi-vacancy clusters. In paramagnetic austenitic steel, the size of vacancy clusters remains unchanged, within the limits of error. An analysis of changes in the value of τ_2 for titanium suggests that above-equilibrium vacancies are produced in the corrosion process. Their concentration depends not only on the direction of the magnetic field penetrating the sample during its corrosion, but also on whether the corrosion occurs directly after annealing, or after a previous aging in a magnetic field. This result proves that in the corrosion process of titanium, the structure of the passive layer on grain surfaces plays a huge role in the formation and migration of vacancies. Assuming that titanium samples previously annealed at various temperatures differ in the morphology of the passive layer, positron annihilation was analysed in corroded Ti(500) and Ti(1100) samples. The intensity I_2 of the defect component is usually smaller in Ti(1100) samples than in Ti(500). This proves the greater uniformity of the passive layer which, as a result of the action of forces of an electromagnetic origin, is more defective and deformed in a parallel field than in a perpendicular one.

Table II shows the relative changes of the τ_2 and I_2 parameters calculated as the difference between the parameters (P) after the corrosion (a) and before the corrosion (b) relative to the parameters prior to the corrosion

$$\frac{\Delta P}{P} = \frac{P_\mathrm{a} - P_\mathrm{b}}{P_\mathrm{b}}, \tag{1}$$

where $P = \tau_2$, I_2. For samples (4) and (6), as the values of P_b, we accepted those that were designated after magneting aging, but before corrosion.

It was noted that the relative change in annihilation parameters depends on whether corrosion occurred for samples (3) and (5) or for samples (4) and (6).

Obviously, changes of I_2 for samples (4) and (6) are generally smaller than for samples (2), (3) and (5). Similarly, the changes of this parameter for samples (5) are smaller than for samples (3). These results suggest that not only the temperature at which the passive layer forms before the corrosion, but also the direction of the magnetic field in which this layer forms may impact the annihilation parameters of the original sample. To check this hypothesis, first the positron lifetime spectra were measured in samples directly after their annealing, and then after their aging in a magnetic field, without a corrosive atmosphere.

TABLE II

Relative changes of parameters of positron lifetime spectra for "direct" corrosion and corrosion after "magnetic aging".

Metal	Orientation of samples in a magnetic field	"Direct" corrosion		Corrosion after "magnetic aging"	
		$\Delta\tau_2/\tau_2$ [%]	$\Delta I_2/I_2$ [%]	$\Delta\tau_2/\tau_2$ [%]	$\Delta I_2/I_2$ [%]
Fe	$B=0$	-2.27 ± 0.35	138.67 ± 8.73	–	–
	$\oplus$	45.76 ± 7.41	234.00 ± 12.48	1.60 ± 0.34	89.72 ± 2.16
	$\|\|$	-1.42 ± 1.85	200.93 ± 11.65	-2.72 ± 0.78	-48.80 ± 1.00
S20	$B=0$	9.86 ± 1.83	364.00 ± 58.24	–	–
	$\oplus$	19.30 ± 5.43	249.20 ± 39.87	5.47 ± 1.69	63.03 ± 2.06
	$\|\|$	8.68 ± 1.76	128.40 ± 22.14	-1.20 ± 0.06	-12.58 ± 4.11
S0H18N9	$B=0$	-12.45 ± 0.10	40.39 ± 0.03	–	–
	$\oplus$	-14.86 ± 4.14	29.80 ± 0.05	0.75 ± 0.6	16.81 ± 0.25
	$\|\|$	-14.70 ± 1.63	34.24 ± 0.16	-0.33 ± 0.13	-8.86 ± 0.13
Ti(500)	$B=0$	0.00	126.73 ± 5.44	–	–
	$\oplus$	0.00	163.63 ± 13.61	0.00	109.91 ± 0.23
	$\|\|$	0.00	169.89 ± 13.07	0.00	9.97 ± 0.96
Ti(1100)	$B=0$	0.00	0.00		
	$\oplus$	0.00	76.10 ± 16.89	0.00	190.16 ± 59.28
	$\|\|$	0.00	122.34 ± 21.65	0.00	2.93 ± 1.83

Figure 3 shows relative changes of parameters of the defect component of the positron lifetime spectrum in the investigated metals caused by aging in a magnetic field of the appropriate orientation. It can be seen that for all analysed metals except Ti(1100), samples aging in a magnetic field causes the intensities of this component to increase $\left(\frac{\Delta I_2}{I_2} > 0\right)$.

This can be interpreted as a result of an increased concentration of defects in near-surface layers penetrated by positrons. The increases in their concentration are greater when metals age in a field parallel to sample surface than if they age in a perpendicular field. We believe that this results from the additional damaging and stressing of the passive layer which can be treated as a material conducting the electrical current of ions and vacancies, placed in a magnetic field. Hence, it can be claimed that the passive layer is more sensitive to formation of larger defects in ferromagnetic materials than in paramagnetic ones. The formed passive layer in the paramagnetic materials is cohesive and more resistant to formation of vacancies.

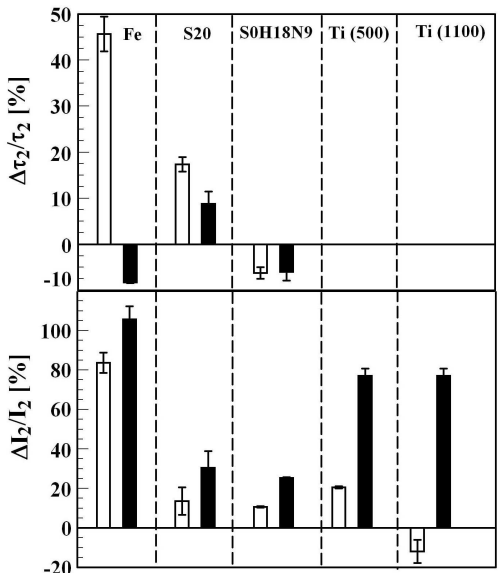

Fig. 3. A diagram of relative changes in the lifetimes ($\Delta\tau_2/\tau_2$) and intensities ($\Delta I_2/I_2$) in Fe, S20, and S0H18N9 steel grades and Ti caused by "aging" in a magnetic field perpendicular (□) and parallel (■) to the surface of the sample without a corrosive atmosphere.

4. Conclusions

The obtained results of the positron lifetime measurements demonstrate that in the near-surface layers of Fe, Ti, as well as S20, and S0H18N9 steel grades additional defects form as a result of corrosion. Corrosion in the presence of a magnetic field causes formation of defect clusters in iron and the steel grades, but in titanium — only increase of vacancy concentrations. The orientation of the external magnetic field relative to the corroding surface of samples influences the concentration of defects produced in the near-surface layer of metal.

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