APPLICABILITY OF POSITRON ANNIHILATION METHODS FOR CORROSION STUDY

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1. Introduction

Positron annihilation spectroscopy is a very sensitive method even for a small change of microstructure. As it is able to determine concentration and size of vacancy-type defects in samples with very low concentration (from 0.1 to 500 ppm) [1], this technique can also observe changes in material after corrosion processes. Corrosion is the destructive attack of a metal by chemical or electrochemical reactions with environment [2], which causes creation of iron oxides in material as well as worsens of material coherence. Therefore, atom binding can be broken and due to this and due to diffusion processes material lattice tries to relax. During the process of relaxation, some new structural defects can be formed. Degradation effect on lattice and its defect presence has already been investigated by Zhang et al. [3] who demonstrated a growth of positron mean lifetime with an increase of chlorine content in environment for duplex (Cr-Ni) austenitic steel. This paper also indicated an increase of defect size and a slightly decease of defect concentration with the increase of chlorine presence in the environment. Further, Pietrzak et al. [4] studied low alloyed steels in vapour of hydrochloric acid at 140 °C. These steels were exposed for 100 hours in this atmosphere and then their vacancy defects were larger and the concentration also increased. These experiments can lead to assumption that our positron annihilation spectroscopy could also see corrosion degradation of our steels.

Steels applied in nuclear facilities have to have very good resistance to corrosion, thus the investigation of the material degradation due to corrosion can be very useful even in condition of microstructural changes. This paper studies applicability of our positron annihilation lifetime spectroscopy as method sensitive to material corrosion and gives a review if it can be practically used for measurement of steels intended for nuclear power plants (NPPs) of 4th generation (GEN IV). Our study was focused on investigation of commercial austenitic steel NF 709. This steel is candidate for construction of pipes, tubes and heat exchangers.

2. Experiment

Experimental samples

NF 709 (Fe-20Cr-25Ni) is an austenitic stainless steel, which belongs to the new alloys appropriate for the new generation of the NPPs. This steel differs from other austenitic steels by its thermal and creep resistance as well as its good ductility [5]. NF 709 was produced by Nippon Steel in Tokyo, Japan. Technological manufacturing of NF709 is divided into following processes: cold-drawing, solution treatment at 1 100°C and finally water quenching [6]. In the structure of NF 709, niobium nitrides (NbN) and sometimes chromium-niobium nitrides (CrNbN) appear. Titanium nitrides (TiN) or titanium-niobium carbides (Nb, Ti) C are not also abnormal in this steel in a view of its chemical composition shown in Tab.1. The samples of the investigated steels were prepared from as-received material by cutting the steel

sheets into suitable pieces. In order to remove surface impurities, the sample surfaces were polished after the milling cutting into a mirror level.

Tab. 1. *Chemical composition of austenitic steel NF 709 (in % wt.).*

Cr	Ni	Mn	Mo	Si	Nb	Ti	N	C	B	P
22.22	25.34	0.92	1.4	0.38	0.24	0.05	0.17	0.03	0.005	0.022

Experimental technique

The samples of NF 709 steel were investigated by positron annihilation lifetime spectroscopy (PALS). The PALS [7] can determine concentration and size of vacancy-type defects in sample from mono-vacancies and dislocation; therefore can describe area where microscopy techniques are not so sensitive. The measuring equipment [8] used in this work consists of two BaF_2 scintillation detectors connected in fast-fast mode. As positron source, ^{22}Na covered in Kapton foil was used. The resulting spectrum was evaluated by program LifeTime9 [9]. The value of FWHM parameter was close to 194 ps. Fit Variant (reduction of chi-square) achieved value in range (1; 1.1).

Experimental treatment

Positron annihilation lifetime spectroscopy investigated changes in microstructure after a corrosion degradation. Firstly, samples in as-received state were studied and then these samples were exposed to corrosion environment. One pair of samples was corroded at Institute of Materials Science in Trnava, where samples were stored for 493 hours in corrosion chamber in a fog from water solution of NaCl at temperature of 35°C. For the second pair of sample, the fast corrosion test was performed during 16 hours bath in hydrochloric acid with concentration of 30%. Corrosion of steels were visible, however significant change of surface was seen only for samples after the fast corrosion test (See Fig.1).
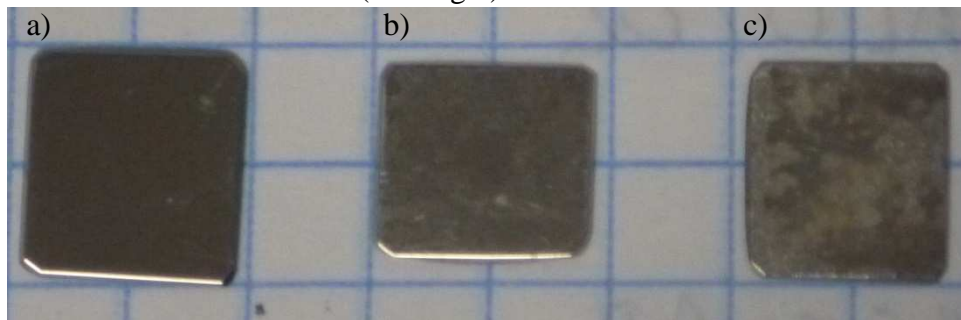

Fig. 1: *Photo of samples before corrosion (a) and after corrosion experiments - in corrosion chamber (b) and after the fast corrosion test (c).*

3. Result and Discussion

PALS spectra were decomposed into three components according to the Standard trapping model [10]. The shortest lifetime (LT1) of NF 709 achieved values between 100 and 106 ps, which describes positron annihilation in bulk. The second positron lifetime (LT2) found within the range from 219 to 317 ps characterizes vacancy type defects and is dependent on the size of three dimensional vacancy clusters Vn consisting n vacancies. The last - third positron component with almost negligible contribution has the largest value describing annihilation in porous layers or in air between sample and positron source.

Values of LT2 are presented and compared each other in Fig.2a. In this graph, the differences of microstructure are demonstrated via the presence of vacancy defects. Also

a)   b)

evident increase of second lifetime due to corrosion (Fig. 2a) was found for all steels as was assumed, which can mean growth of defects. The intensity of second component deceased (Fig. 2b). It can indicate lower concentration of larger defects than in as-received state. First lifetime slightly increased from 100 ps to 103 and 106 ps; therefore previously existed smaller defects could be included in this component.
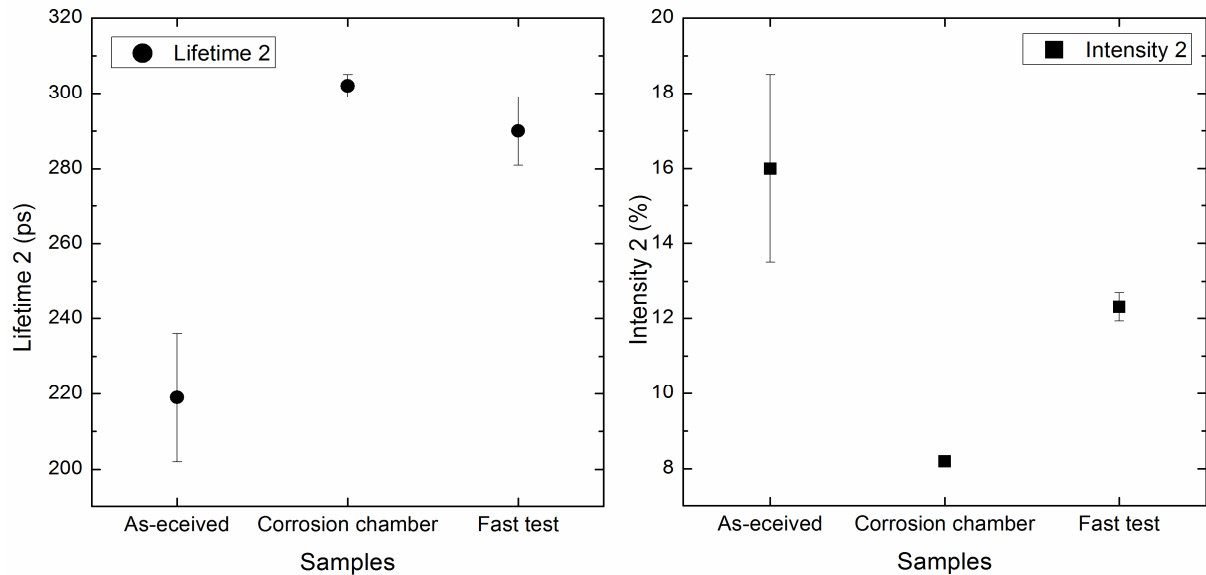

Fig. 2: *PALS results: positron lifetimes describing defect size (a), intensity of positron annihilated in defects proportional to defect concentration (b).*

As-received sample contains combination of di- and three-vacancies in predominance, while corroded samples probably five-vacancies after fast corrosion test and six-vacancies after the corrosion in the chamber.
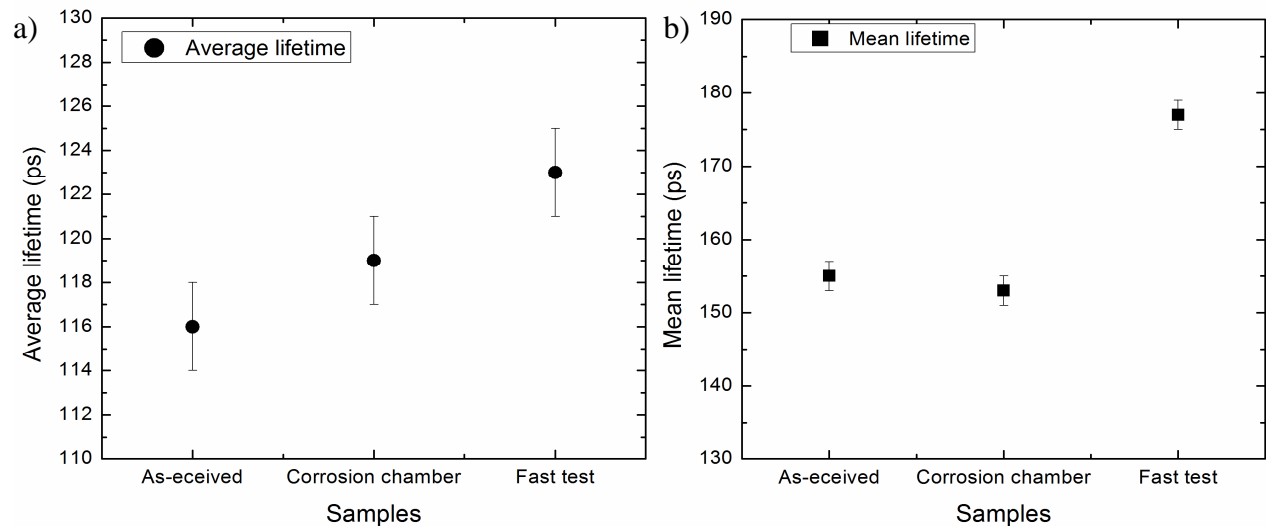

Fig. 3: *Mean lifetime and average lifetime values.*

The values of mean lifetimes (Fig. 3a) are almost the same if we compare as-received sample (155 ± 2 ps) and corroded one in the chamber (153 ± 2 ps). These values are the same in term of error bars. However, the sample corroded in the fast corrosion test has mean lifetime with a value of 177 ± 2 ps. Mean lifetime is loaded also with the non-significant 3rd positron component which can be influenced by sample - source position during preparation of measurement. Thus, the average positron lifetime calculated from 1st and 2nd components can give more visible change between different states of samples (Fig. 3b). The average lifetime is

the smallest for as-received sample (116 ps) which demonstrate the smallest presence of vacancy defects. This is followed by average lifetime for sample corroded in the chamber (119 ps). The sample after the fast corrosion test probably contains the most defects as its average lifetime is the highest - 123 ps.

4. Conclusion

Our measurements of austenitic steel NF 709 by positron annihilation lifetime spectroscopy demonstrated a change of microstructure after both corrosion experiments. However the corrosion process in the corrosion chamber was very small, the fast corrosion test showed degradation of material as positron mean lifetime increased and a material surface also changed its colour from typical silver one to black one. This indicates presence of oxides in the surface in high concentration, which could be observed by microscopy methods in further work. The sample exposition in the hydrochloric acid, even for shorter time, was more degrading than longer exposition in NaCl water vapour. Thus, these results can point out that although steel NF 709 can corrode in extremely corrosive conditions, this steel is enough corrosion resistant to common corrosion environments. This study also gives a first proof that our device of positron annihilation lifetime spectroscopy can recognize structural degradation of materials due to corrosion processes.

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