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MEASUREMENTS OF POSITRONS LIFETIMES IN CORRODED NICKEL

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An attempt was undertaken at making use of a technique of taking measurements of lifetimes of positrons emitted from ^{22}Na source to investigate corroded nickel. It was found that after corrosion in HCl vapours mean positrons lifetime, the second component of positrons lifetimes as well as its intensity rise along with the corrosion time.

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1. Introduction

It is over twenty years now that the nuclear method of conducting investigations into defects in the volume and on the surface of solids, based on positron annihilation phenomenon, has been developing on a quite intensive scale [1-3]. The present work is an attempt at adopting positron annihilation to investigations of the phenomenon of pitting corrosion in metals. Pitting occurs mainly in environments containing chlorides and affects metals and alloys covered with passivating oxide layers. Research carried out for many years by the use of various methods has proved that pittings, which could — after some time — take sizes as large as the tenth of the millimeter order, are formed in the physically and chemically defected surface layer or the one close to the surface.

Kinetics of formation of pittings has not been known thoroughly yet. It seems that in examinations of the first stages of corrosion, the method of measuring lifetimes of monoenergetic positrons implanted into investigated samples could be very effective. However, the quantitative analysis of dependence of the number of positron annihilation acts on the depth from the surface into which they penetrate shows that the quanta originating from positron annihilation from ^{22}Na source in nickel carry, in their majority, the information concerning the layers close to the surface. Because of this an attempt was made to apply the technique of measuring lifetimes of positrons emitted from radioactive ^{22}Na source to investigations into kinetics of pitting in nickel. An assumption was made here that the spectrum of lifetimes reflects the presence of small dimension defects on which macroscopic pittings are formed during the process of corrosion.

2. Preparation of samples for investigations

Samples cut out of nickel tinware of 99.9% purity were used for the investigation. Before corrosion, the samples were cleansed in methanol and then heated in vacuum at 900 K for 3 hours and then slowly cooled (~ 2 K/min) to meet room temperature. For each of the heated samples a spectrum of positrons lifetimes was obtained. Then the samples were hung in a closed vessel, on the bottom of which was a 50% water solution of hydrochloric acid. In the atmosphere saturated with HCl vapours, the samples were corroded for the period ranging from 4 to 144 hours. After this time the measuring of lifetimes of positrons in corroded nickel was carried out again.

Some of the heated samples were corroded in a 50% water solution of HCl or in a 50% solution of H_2SO_4 by passing current of 2.3×10^{-2} A/m² density through the solution during the time from 0.5 to 4 hours while the examined solution was the anode. Both the corrosion and measurements of lifetimes were examined at room temperature.

3. Results of measurements and their interpretation

Figure 1 shows dependence of positrons mean lifetime in corroded nickel on the time of storing samples in the corrosive atmosphere of HCl. It is clear that the mean positrons lifetime in unit thus corroded grows in a systematic way from the value of 122 ± 5 ps before the beginning of the corrosion — up to 244 ± 7 ps after 144 hours of the process. The obtained result proves that in the investigated system there occur changes connected either with concentration and sizes of the defects or with a chemical change of superficial nickel oxide NiO into hydrated nickel chloride $\text{NiCl}_6 \cdot 6\text{H}_2\text{O}$. The distribution of lifetimes spectrum into two components shows that the second component τ_2 rises systematically along with the growth in time of keeping nickel in the corrosive atmosphere, changing from 245 ± 5 ps for

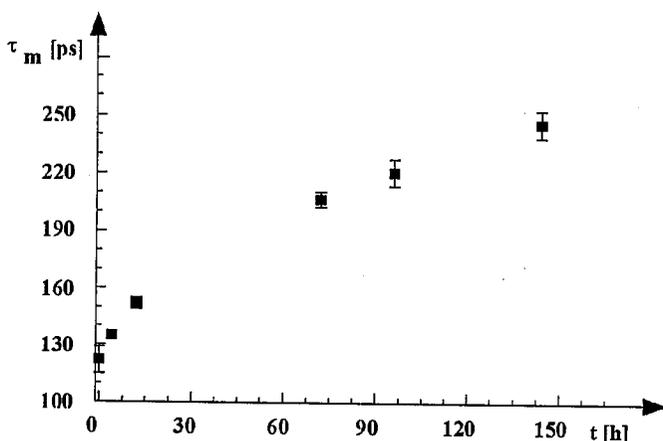


Fig. 1. Dependence of positrons mean lifetime in corroded nickel on time of exposure of samples in 50% HCl solution vapours.

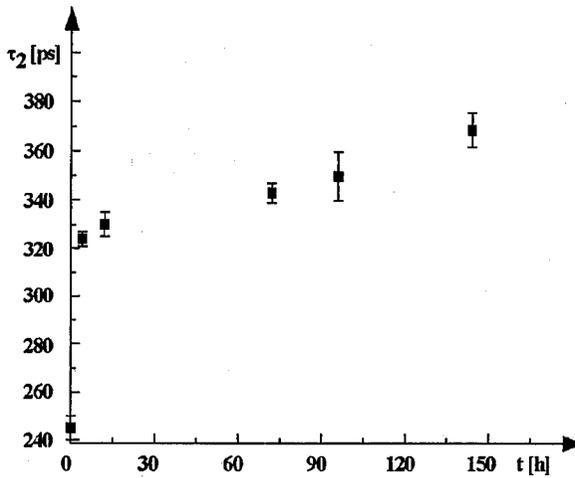


Fig. 2. Dependence of the second component of positrons lifetime in corroded nickel on time of exposure in 50% HCl solution vapours (room temperature).

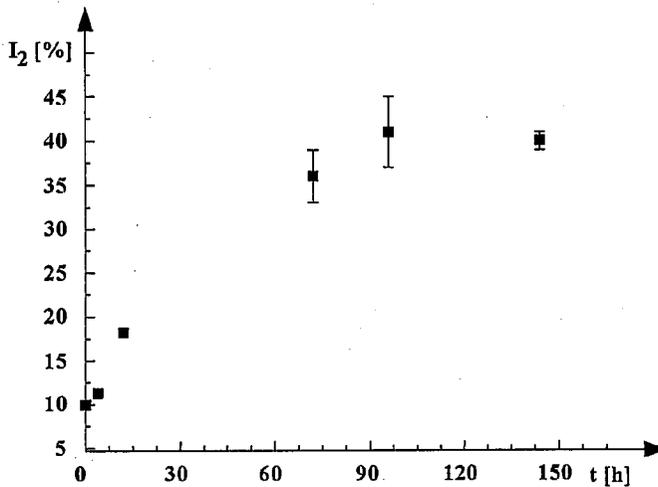


Fig. 3. Dependence of intensity of the second component of positrons lifetime in corroded nickel on time of exposure in 50% HCl solution vapours (room temperature).

heated samples to 369 ± 7 ps (Fig. 2). There also rises the intensity of the second component from 10% for low-corroded samples to 40% for ones after 144 hours exposure to corrosion (Fig. 3). The obtained result suggests that it is likely that both concentration of defects trapping positrons and their dimensions increase in the layer close to the surface. If one were to assume that it is annihilation in defects that is responsible for the value of the second component of positrons lifetime, then the value of time τ_2 would indicate that they are clusters of dimension ranging from several to several tens of vacancies.

TABLE I

Influence of corrosion manner on annihilation parameters of nickel (room temperature).

Annihilation parameters	τ_m [ps]	τ_2 [ps]	I_2 [%]	χ^2
Heated nickel (before corrosion)	122 ± 5	245 ± 5	10.0 ± 0.5	1.020
Corroded nickel for 4 hours in vapours 50% HCl	135 ± 1	324 ± 3	11.3 ± 0.1	0.997
Anode corroded nickel for 4 hours in 50% HCl solution	139 ± 7	345 ± 4	12.3 ± 0.1	0.962
Anode corroded nickel for 4 hours in 50% H ₂ SO ₄ solution	138 ± 4	269 ± 3	18.9 ± 0.3	1.023

Influence of the manner of corroding on positrons lifetimes spectrum is presented in Table I. It contains mean lifetime τ_m values of component τ_2 and its intensity I_2 for nickel samples exposed to corrosion for 4 hours in room temperature:

- (a) before corrosion,
- (b) in vapours of a 50% HCl solution,
- (c) anodically in 50% HCl solution,
- (d) anodically in a 50% H₂SO₄ solution.

It is evident that all the parameters of positron lifetimes in nickel corroded in HCl remain close to one another irrespective of the fact whether the exposure was carried out in HCl vapours or anodically in a solution of this compound. However, annihilation parameters for nickel anode corroded in a 50% solution of H₂SO₄ differ distinctly from the parameters obtained for nickel corroded in HCl, but come close to annihilation parameters for non-corroded nickel. Nonetheless, as it is well known from the literature of the subject, pitting corrosion is largely limited in sulphate solutions. This is probably connected with the fact that sulphate salts being much harder soluble than chloride ones partly block nickel surfaces in a mechanical way. It appears that the obtained results of measurements of positrons lifetimes confirm the above point of view.

Table II presents results of measurements of positrons lifetimes for nickel:

- (a) before corrosion,
- (b) after 144 hours of corroding in HCl vapours,
- (c) after flushing the layer of NiCl₂ · H₂O, which covered the surface of metal, with a stream of water.

The results shown in Table II point to a strong trapping of positrons in corroded nickel layer because after the corroded layer becomes rinsed out the

TABLE II

Annihilation parameters for nickel.

	τ_m [ps]	τ_2 [ps]	I_2 [%]	χ^2
After heating in 900 K (before corrosion)	121 ± 5	259 ± 21	7.0 ± 2	1.023
After corrosion for 144 hours in vapours 50% HCl	244 ± 7	369 ± 7	40 ± 1	1.085
After rinsing corrosion layer	115 ± 6	218 ± 22	11 ± 3	1.013

annihilation parameters for nickel are — within limits of error — brought closer to the ones for nickel before corrosion.

It follows from the above presented results that the second component τ_2 in spectra of lifetimes of the examined samples is therefore connected with positron annihilation in the strongly defected brittle layer of nickel close to the surface. A full explanation of the obtained results requires carrying out additional examinations.

4. Conclusions

The conclusions presented below follow from the conducted investigations:

- mean positrons lifetime, the value of the second component and its intensity in spectrum of the lifetime increase together with the growing time of keeping nickel samples in HCl environment;
- after the same length of corrosion time in HCl environment the annihilation parameters of the unit remain close to one another, irrespective of the manner of exposure to corrosion;
- after the same length of corrosion time in H_2SO_4 environment the annihilation parameters take on lower values than the ones after exposure to corrosion in HCl;
- despite a number of limitations the technique of taking measurements of lifetime of positrons emitted by radioactive ^{22}Na isotope may be applied to investigations of corrosion process in metals.

References

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