INVESTIGATIONS INTO THE INFLUENCE OF HYDROGEN AND DEFECTS ON THE SPECTRA OF LIFETIME OF POSITRONS IN PALLADIUM

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The influence of interstitial hydrogen concentration and structural defects caused by quenching of palladium, begun at different temperatures up to the temperature of liquid nitrogen or by stretching by external forces, on spectra of lifetimes of positrons in this metal was investigated. It was found that the spectra of positron lifetimes in the examined systems are best described by their distribution into two components. On the basis of the two-state model of annihilation, the conclusion was drawn that the initial temperature from which quenching of palladium is commenced and also the relative elongation, which is caused by external forces, markedly influence the concentrations and sizes of defects in the sample.

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1. Introduction

Getting to know all the mechanisms of interaction between hydrogen and metals and their alloys has, for many years now, been a subject of interest held by physicists, chemical engineers, or material engineers. The problem interests also specialists in the fields like power engineering, petroleum chemistry, metallurgy, and nuclear physics. Normally, hydrogen in metals leads to worsening of many physical properties, including mechanical, electrical and magnetic ones [1]. Among others, this facilitates formation and development of cracks. In recent years this has been the cause of a number of failures and disasters [2–5] and still is responsible for a lot of material damage. For this reason, it is very important to learn about the mechanisms of the interaction between hydrogen and defects of the crystalline structure. Investigation into these processes has a fundamental sense in learning about causes behind changing physical properties and finding means to control the destructive activity of hydrogen, for instance, with reference to mechanical properties of industrial constructions and machinery. Unfortunately, up to date the relation between microscopic processes of deformation and their macroscopic properties has not been known sufficiently enough. Despite this, metal–hydrogen

(455)

systems have been widely used in many branches of technology and industry. Furthermore, it is for many reasons, including technical, economic, and ecological ones, that the share of metal–hydrogen systems is predicted to rise considerably in the world economy [6, 7]. Although the ability of palladium to absorb great amounts of hydrogen and to rapidly diffuse in it has been known for over a hundred years, there is not much information, in the literature of the subject, on the properties of defects in this material and their interaction with interstitial hydrogen [8].

The present paper is devoted to investigations of the influence of the way of defecting palladium (through quenching or stretching by external forces) and also of concentration of hydrogen on spectra of lifetimes of positrons in this metal. A qualitative analysis of the obtained results has been done to determine changes in the concentration and sizes of defects induced by quenching and stretching of palladium.

2. Preparation of samples for investigation

Spectra of lifetimes of positrons in palladium and Pd–H systems of different degree of defectiveness were examined. A fast-slow annihilation spectrometer of 210 ps resolution was used in the investigation. ^{22}Na isotope placed between two identical samples in a "sandwich" system served as the source of positrons. The analysis of the spectra was done with the use of LIFETIME program. All the examined samples were first annealed in the vacuum (the pressure lower than 10^{-6} Pa) at 1123 K during three hours and afterwards slowly cooled (1 K/min) to the room temperature.

Defecting samples by quenching was carried out after their repeated annealing at 973, 1173, and 1373 K, respectively, during three hours, followed by subsequent rapid cooling to the temperature of liquid nitrogen.

Samples were electrolytically hydrogenated to a determined concentration at the room temperature. The sample being hydrogenated (negatively polarized) was placed in 0.1 n H_2SO_4 solution in a Hoffmann apparatus, between two flat platinum anodes. A detailed description of the hydrogenation conditions and the manner of determining the hydrogen concentration in the sample can be found in [9]. The samples were hydrogenated following their quenching.

In the investigations into the influence of external stresses on the positron lifetimes spectra, the annealed samples (pure or hydrogenated to the same concentration), of the same degree of defectiveness and a positrons source placed between them, were fixed in the device which allowed stretching them within the limits up to 5% of the initial length. Additionally, changes in the electric resistance and internal stress in dependence on the elongation were measured. All the lifetimes spectra were examined at the room temperature.

3. Results of the investigation and their interpretation

The obtained spectra of positron lifetimes in the examined samples were analyzed through their distribution into one, two, or three components. An analysis

of the results points to the fact that the best value of the fit test coefficient (χ^2) is achieved with the distribution of positron lifetimes spectrum falling into two components of τ_1 and τ_2 and intensities I_1 and I_2, respectively. In the two-state annihilation model, which assumes that positrons which penetrate into the substance, annihilate from the free state or the one localized in one type of defects, component τ_2 of the positron lifetimes spectrum corresponds to the mean positron lifetime in defect, whereas its intensity is connected with the concentration of defects in the sample through the following dependence:

$$I_2 = \frac{\mu C_\mathrm{d} \tau_2 \tau_\mathrm{f}}{\tau_2 - \tau_\mathrm{f} + \mu C_\mathrm{d} \tau_2 \tau_\mathrm{f}}, \tag{3.1}$$

where μ — coefficient of positron capture by defects (its value depends on the sizes of the defects), C_d — concentration of defects in the sample, τ_f — free positron lifetime in the sample

$$\tau_\mathrm{f} = \frac{\tau_1 \tau_2}{I_1 \tau_2 + I_2 \tau_1}. \tag{3.2}$$

The changes in the mean lifetime of positrons in sample τ_m

$$\tau_\mathrm{m} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2} \tag{3.3}$$

are popularly interpreted as a result of changes in the percent share of annihilation of positrons trapped in defects. Both the results of theoretical and experimental investigations point to the fact that the mean lifetime of positron in defects (in the two-state model: τ_2) depends, among others, on the sizes of the defect. Due to a decreasing concentration of electrons in the defect, the longer the positron "lives" in it, the greater the linear sizes of the defect.

Thus, the changes in the intensity of the second component of the positron lifetimes spectrum, I_2, in the examined system, are a certain measure of defects concentration as long as their sizes do not change too evidently.

3.1. Results of the investigation referring to quenched samples

3.1.1. Influence of the initial temperature of quenching

Figure 1 presents dependence of lifetimes of components τ_1, τ_2 and mean positrons lifetime in sample τ_m on initial temperature T_0, from which quenching was started. At the same time Fig. 2 shows the dependence of intensity of the second component of positron lifetimes spectrum on temperature T_0. On the basis of a two-state annihilation model one may, in the first approximation, assume that the higher the temperature from which quenching of palladium is begun, the greater the sizes of defects which develop as a result of this process, though their concentration is lower. Results of the research into resistivity and annihilation conducted prior [10–13] indicate that over 35 K, the Frenkl vapors in palladium become extremely mobile and undergo recombination, whereas over 450 K it is the non-equilibrium vacancies and dislocations that recombine. Thus, rapid cooling of palladium to temperatures higher than 970 K causes equilibrium vacancies to combine in defects of greater sizes. In case of iron and aluminum, the values of component τ_2 we obtained for palladium, are interpreted as lifetimes of positrons in several- or even dozen-plus-vacancy clusters. Since the mobility of vacancies
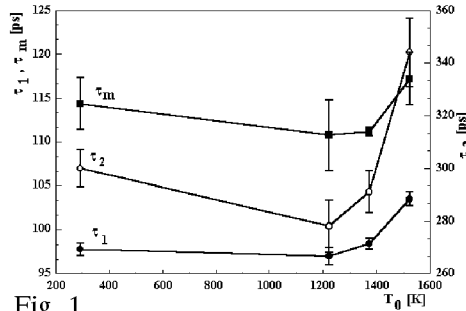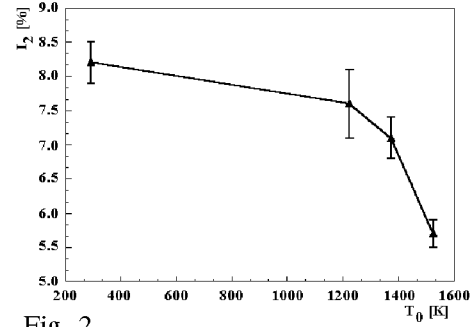
Fig. 1.   Dependence of mean lifetime of positrons τ_m, values of components τ_1, τ_2, spectra of positron lifetimes on initial temperature T_0, from which quenching of palladium was begun.

Fig. 2.   Dependence of the intensity of the second component of the spectrum of positron lifetimes I_2 on the initial temperature of quenching.

depends on temperature of the sample, it may be supposed that the speed of conglomeration and cluster sizes grow together with temperature T_0 from which quenching was begun.

3.1.2. Influence of hydrogen concentration

In order to learn about the interaction of interstitial hydrogen with defects in palladium, for the further investigation, the following two pairs of samples were chosen:

- annealed but not quenched;
- quenched, beginning at 1570 K initial temperature.

Both pairs of the samples were successively hydrogenated to the concentrations of 0.02, 0.04, 0.07, and 0.1 at.H/at.Pd, respectively. Before commencing and after each hydrogenation, spectra of lifetimes of positrons in both types of the samples were examined. Figures 3, 4, and 5 present, respectively, the dependence of mean lifetime of positrons τ_m, component τ_2, and its intensity I_2 on hydrogen concentration for annealed samples (curves a's) and quenched ones (curves q's). On the basis of the results represented in these graphs and in Fig. 1, a conclusion may be drawn that despite slow cooling, non-hydrogenated samples, accepted by us to be annealed, do contain some non-equilibrium defects in the form of multi-vacancy clusters. Their sizes are, however, on the average, smaller than the ones in non-hydrogenated quenched samples. Their concentration is also smaller. Introducing hydrogen of concentration smaller than 2% into both types of samples causes lowering the value of component τ_2 and a rise in its intensity. This means that introduction of a small amount of hydrogen into palladium results in disintegration of clusters into smaller ones. Keeping on adding hydrogen up to the concentrations from 0.04 to about 0.07 at.H/at.Pd in annealed samples causes positrons to annihilate in defects of greater sizes and their percent share in annihilation rises inconsiderably. This can mean that hydrogen in the sample containing multi-vacancy clusters readily occupies defects of smaller sizes. In con-
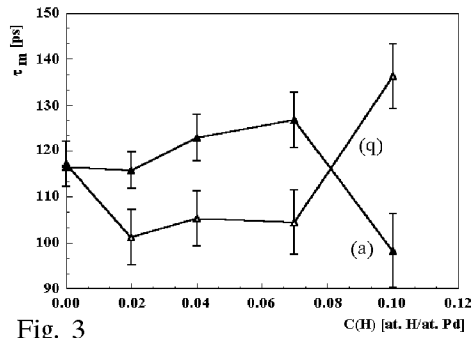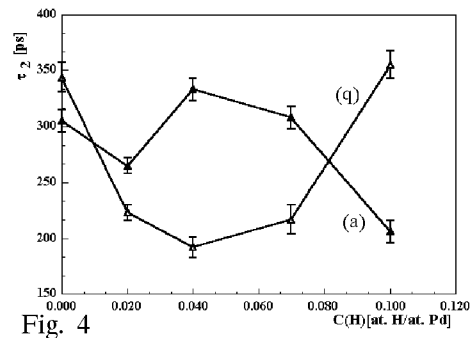
Fig. 3. Dependence of mean lifetime of positrons on hydrogen concentration for annealed (*a*) and quenched (*q*) samples.

Fig. 4. Dependence of the value of component τ_2 of the spectrum of positron lifetimes on hydrogen concentration for annealed (*a*) and quenched (*q*) samples.
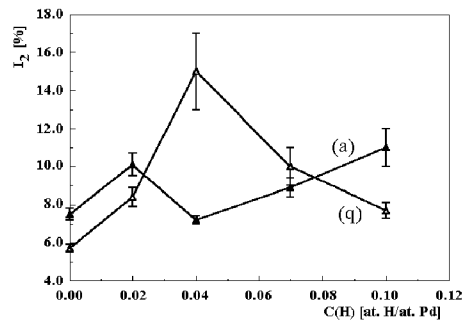

Fig. 5. Dependence of the intensity of the defective component of the spectrum of positron lifetimes on hydrogen concentration for annealed (*a*) and quenched (*q*) samples.

trast, introducing hydrogen into quenched samples in the above-discussed range of its concentrations causes positrons to annihilate in defects, whose sizes are smaller and their concentration is greater than in the non-quenched samples of the same concentration of hydrogen. This means that in this range of concentrations, hydrogen in quenched palladium brings about disintegration of clusters into smaller ones. When the concentration of hydrogen in palladium reaches the value of 0.1 at.H/at.Pd, positrons which have been trapped, annihilate in defects of smaller sizes while their concentration rises. On the other hand, in hydrogenated quenched samples, the sizes of the defects trapping positrons are now greater than at lower hydrogen concentrations. They are also greater than the ones of the "annealed" samples hydrogenated up to the same concentration. This may be caused by a repeated connecting of smaller clusters into bigger ones.

As can be seen, the analysis of positron lifetimes points to complex mechanisms of interaction between hydrogen atoms and defects developed through quenching of palladium. The above analysis does not include the possibility of

de-trapping of positrons from extensive defects. It does not take into account the change in the phase composition at a change in hydrogen concentration. Within the examined range of hydrogen concentration in annealed palladium, the share of beta phase alters within the bounds from zero to 3%. A full explanation of these aspects of the investigation requires conducting additional experiments.

3.2. The influence of stretching with external forces

In Figs. 6, 7 and 8, respectively, there was shown a dependence of mean lifetime of positrons τ_m, the value of component τ_2, and its intensity I_2 on relative elongation of sample $\varepsilon = \Delta l / l_0$ (l, l_0 — length and initial length of the sample, respectively) for non-hydrogenated palladium (curve a) and the one hydrogenated to the concentration $C_H = 0.06$ at.H/at.Pd (curve b). The presented results indicate that stretching of samples by external forces leads to an increase in the fraction of positrons annihilating from the combined state.
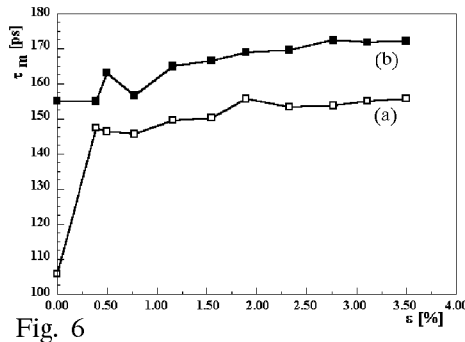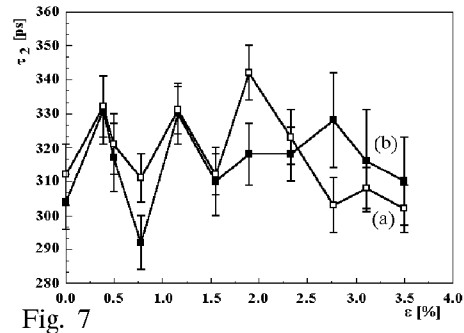

Fig. 6.   Dependence of mean lifetime of positrons on relative elongation of the sample, for Pd (a) and PdH$_{0.06}$ system (b).

Fig. 7.   Dependence of the value of component τ_2 of the spectrum of positron lifetimes on relative elongation of the sample, for Pd (a) and PdH$_{0.06}$ system (b).
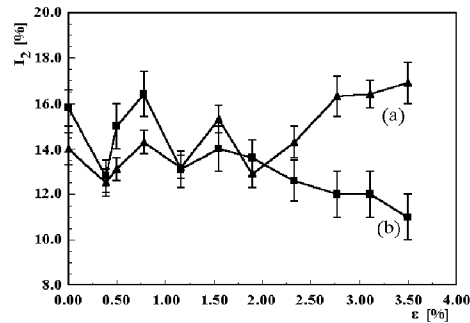

Fig. 8.   Dependence of the intensity of the defective component τ_2 of the spectrum of positron lifetimes on relative elongation of the sample for Pd (a) and PdH$_{0.06}$ system (b).

Changes in the value of the second component of the spectrum of lifetimes of positrons τ_2 and its intensity I_2 both in pure palladium and in hydrogenated palladium point to complex processes of disintegration and combination of defects. In order to facilitate making a fuller interpretation of the obtained results, additional extensometric investigations were carried out and so were examinations of changes in the resistivity in dependence on accretion of the length of the sample (Figs. 9 and 10). It results from the investigations that the area of proportional elastic strains is situated within the range of relative extensions from zero up to about 0.62%. The range of limited proportionality and the range of plasticity, as it follows from the curve of the dependence of resistivity on the relative extension, can be divided into at least two areas of relative extensions:

a) from 0.62% to about 1.96%, in which extension takes place through a slide of interstitial planes, and

b) over 1.96%, in which extension occurs through the so-called twinning connected with a re-orientation of microcrystals and development of the so-called limits of twinning.
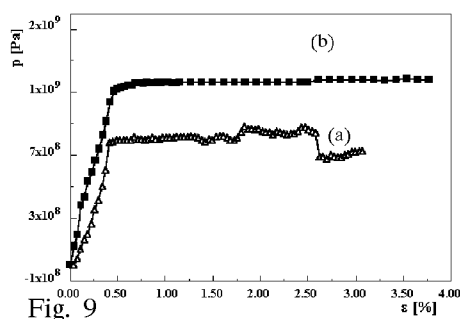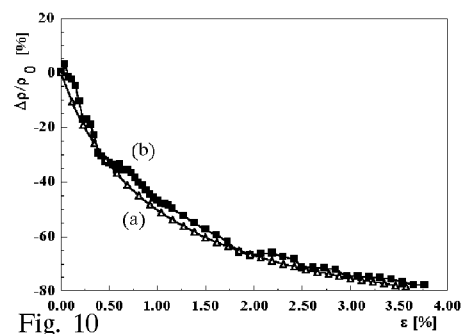

Fig. 9.   Dependence of the internal strain on relative elongation of the sample, for Pd (a) and PdH$_{0.06}$ system (b).

Fig. 10.   Dependence of relative changes in resistivity on relative accretion of length (including changes in the thickness and width), for Pd (a) and PdH$_{0.06}$ system (b) (ρ_0 — resistivity of non-stretched sample).

From the presented results of the annihilation investigations of this part of the research, it follows that in the area of elastic strains, both Pd and Pd–H system contain a certain amount of several-vacancy clusters, whose sizes and concentration, in both systems under examination, are approximately the same and independent of the relative extension. In range (a) of plastic deformations of non-hydrogenated palladium, the sizes of clusters, in which positrons annihilate, are already bigger than in the area of elastic strains and approximately the same as in Pd–H system. However, in hydrogenated palladium, their concentration is smaller than in palladium which does not contain hydrogen. Most probably, in part of them, hydrogen atoms were trapped and thus became unapproachable to

positrons. It may also be supposed that within this range of relative extensions, in both systems, there occur processes of connecting and disintegration of clusters.

In area (*b*) of plastic strains ($\varepsilon > 1.96\%$) the concentration of clusters in non-hydrogenated palladium rises considerably and their sizes visibly decrease, most likely due to their dissociation into smaller ones. On the other hand, in hydrogenated palladium, within the range of plastic strains connected with twinning, the sizes of the clusters which occur in it, within the limit of error, do not change during extension. Because of that, as a result of hydrogen being trapped in them, the concentration of clusters available to positrons decreases.

A full explanation of this part of the research requires yet additional experiments.

4. Conclusions

The investigations which were carried out, yield the following conclusions:

— the concentration and sizes of clusters in palladium, which develop as a result of quenching, depend on the initial temperature from which the quenching is begun;

— in Pd–H systems the sizes of the non-equilibrium defects depend on the hydrogen concentration in palladium;

— introduction of hydrogen of a small concentration into palladium causes multi-vacancy clusters to disintegrate into smaller ones;

— in quenched palladium samples which contain greater amounts of hydrogen, positrons annihilate more often in defects of greater sizes than in annealed samples which contain the same amount of hydrogen;

— the size of the elastic strain in Pd and $PdH_{0.06}$ system does not influence the sizes and concentration of clusters, in which positrons annihilate;

— within the range of elastic strains in Pd, which are induced by a slide of interstitial planes, the sizes of clusters, in which positrons annihilate, are greater than in the area of elastic strains and, approximately, are the same as the ones in $PdH_{0.06}$, but their concentration is greater than in hydrogenated palladium;

— in the area of plastic strains of palladium, connected with twinning, stretching causes disintegration of clusters into smaller ones;

— in $PdH_{0.06}$ system, in this ranges of strains, elongation of the sample causes the interstitial hydrogen to migrate to clusters.

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