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## STUDY OF POLYMER/METAL COATING UNDER STRESS USING POSITRON ANNIHILATION SPECTROSCOPY

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**Abstract**—Positron annihilation spectroscopy (PAS) has proven to be a very useful technique for, e.g., the study of defects in materials and the characterization of polymer free-volume. Positron lifetime, Doppler broadening of the annihilation radiation (characterized by the so-called  $S$  parameter) and angular correlation of annihilation radiation (ACAR) are the techniques used mostly. In the last few years these techniques have been extended to the study of physical defects at the atomic level of coating systems. These studies show that positron lifetime and the  $S$  parameter can monitor the degradation of the coating due to environmental changes (water or UV exposure). The present work is focused on the behavior of coatings under external stresses as studied by PAS. Results of positron annihilation measurements (before and after stretching) on interstitial free (IF) steel coated with epoxy using the Delft variable energy positron (VEP) beam facility are discussed. © 2000 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

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### 1. INTRODUCTION

The application of positron annihilation spectroscopy for studying the degradation of polymeric coatings has been described by several authors [1–5]. The results of positron annihilation lifetime spectroscopy (PALS) and Doppler broadening of the annihilation radiation (DBAR) techniques are discussed. In those articles excellent correlation was observed between positron annihilation parameters and the properties of the coatings. Leidheiser *et al.* [1] show a relation between the positron lifetime and the barrier quality of epoxy coatings on steel in an acid environment. In poor barrier coatings larger voids will be present at the metal/coating interface that can be detected by a high value of  $\tau_3$  (longest positron lifetime). The effect of water saturation on the coatings was studied by Mandani *et al.* [3] and MacQueen *et al.* [4] using PALS and by Nielsen *et al.* [5] using DBAR in a positron beam system. The UV irradiation effect was studied using DBAR by Cao *et al.* [2] and showed a significant decrease in the  $S$  parameter ascribed to the

degradation of the polymers caused by the exposure and a correlation was found with free radical formation.

Apart from weathering effects, some other properties of the coatings are of interest. For example, mechanical properties and the behavior under stress of the polymer on the metal systems are very important for the so-called on-line coatings. The quality of the polymer adhesion to the metal is crucial for such applications. In this paper we present the first results of DBAR positron beam analysis measurements dealing with interstitial free (IF) steel samples coated with two types of epoxy and subjected to external tensions. The samples were strained by up to 35% of their original length resulting in plastic deformation.

### 2. EXPERIMENTS

#### 2.1. Sample preparation

The samples studied were two different types of epoxy-based polymer. The first (type 1104) was a solid epoxy with an epoxy equivalent weight, EEW (=ratio between molecular weight and the amount of epoxide groups), of 950, while the second (type 828) was a standard liquid epoxy with an EEW of 190. The epoxies were dissolved in a 10% solution of organic

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solvent (acetone). Then they were cross-linked with a Lonzacure M-DEA amine with an active hydrogen equivalent weight, AHEW (=ratio between molecular weight and the amount of active hydrogen), of 77.5, spin-coated on IF steel samples and cured at 150°C for 2 h. The steel substrates (1 mm thick) were polished with a diamond paste (7 μm), annealed for 2 h at 1000 K and finally electro-polished to provide a smooth defect free and flat surface to the coating. The thickness of the coating layer was determined by positron beam analysis. The Laboratory of Coatings Technology in Eindhoven provided both epoxy samples and the amine.

### 2.2. Positron annihilation experiments

The positron annihilation experiments were performed with the Delft variable energy positron beam (VEP) [6, 7]. The positrons were injected in the samples with energies tuned between 100 eV and 25 keV. Energy spectra of the annihilation radiation around the 511 keV peak were recorded with a single Ge solid-state detector as a function of the positron implantation energy. All experiments were carried out at room temperature under a vacuum of about 10<sup>-6</sup> Pa. The data were analyzed with the VEPFIT program [8].

### 2.3. Tensile experiments

A tensile/compression substage from Kamrath & Weiss GmbH sited in the Materials Science Center of the University of Groningen was used to strain the coated samples. The cross-sectional area of the samples was 2.5×0.9 cm<sup>2</sup> and loads from 0.3 up to 3 kN were applied to the samples in order to obtain strains ranging from 1 to 35% of the original length. The strain rate of the experiments was 5 μm/s.

## 3. RESULTS AND DISCUSSION

Measurements of the Doppler broadening of the positron-electron annihilation radiation are generally characterized by the  $S$  (shape) parameter, defined as the ratio between the central part of the annihilation spectra and the total spectra. This parameter reflects the positron annihilation with valence electrons (low momentum). In general, a high value of  $S$  indicates positron annihilation in open volume defects. If the material allows the formation of a positronium state (Ps), this will contribute to the DBAR with a narrow component because of the low intrinsic moment of the positronium. A second useful parameter for the analysis of DBAR is the  $W$  (wing) parameter, which reflects the positron annihilation with high momentum electrons (core electrons). Figure 1 schematically shows the definition of both parameters and the energy windows  $\Delta E_S$  and  $\Delta E_W$  set to define the integration areas. In the study of interfaces, both parameters can be combined in  $S$ - $W$  maps with a third variable (i.e., implantation energy, temperature, strain...) as a running parameter. These maps are use-

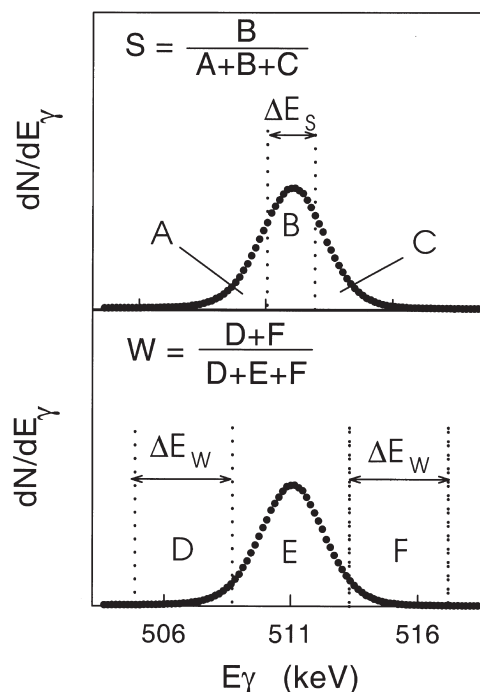


Fig. 1. Schematic definition of shape parameter  $S$  and wing parameter  $W$  of the 511 keV annihilation photopeak. The  $S$  parameter is defined as the area  $B$  (defined by the energy window  $\Delta E_S$ ) divided by the total area  $A+B+C$ . The  $W$  parameter is defined as the area of the wings  $D$  and  $F$  (defined by the energy window  $\Delta E_W$ ) divided by the total area.

ful to trace positron trapping in, e.g., layers as in the samples described here. In general, the measured  $S(E)$  and  $W(E)$  are a sum of the characteristic  $S_i$  and  $W_i$  values of the trapping layers weighted by the fraction of positrons trapped in each layer  $f_i(E)$ :

$$S(E) = \sum_{i=1}^N f_i(E) S_i \quad (1a)$$

$$W(E) = \sum_{i=1}^N f_i(E) W_i \quad (1b)$$

with  $N$  the number of trapping layers.

The analysis of the data is done with the aid of the VEPFIT [8] program. This program provides an algorithm that simulates the implantation and solves the diffusion equation, taking into account the trapping and annihilation of the positrons in the material. The samples studied here are described as a stack of positron trapping layers characterized by a thickness ( $D$ ),  $S_i$  and  $W_i$  parameters and a positron diffusion length ( $L_i$ ).

In Fig. 2 the  $S$  parameter of epoxy-coated samples is plotted against the positron implantation energy. Very similar behavior is observed in both samples with a slightly lower  $S$  parameter for the 828 epoxy.

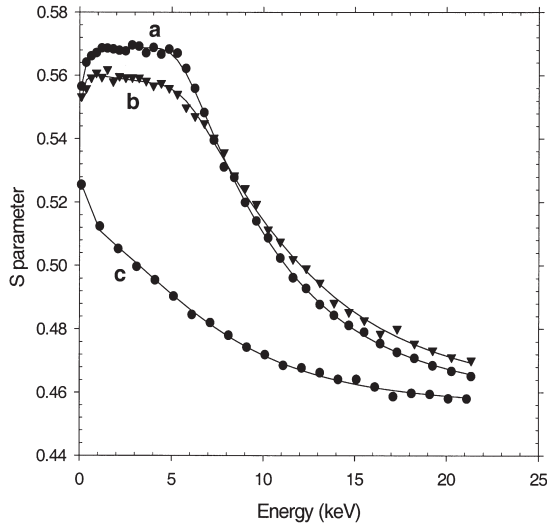


Fig. 2.  $S$  vs positron implantation energy curves for an IF steel sample coated with: (a) epoxy 1004 (solid), (b) epoxy 828 (liquid). Both curves are compared with (c) IF steel without coating. Continuous lines show the VEPFIT results.

For low implantation energies, there is first an increase in  $S$  followed by saturation until approximately 5–6 keV. The high value of  $S$  is attributed to the formation of positronium in the epoxy layer and the following saturation indicates the short diffusion length of the positrons inside the polymer, due to its amorphous state. For a short diffusion length, positrons implanted in the material will not diffuse back to the surface. At energies higher than 5–6 keV a decrease in the  $S$  parameter is observed approaching the value of uncoated IF steel. This change in the  $S$  parameter determines the boundary of the epoxy layer and can be used to determine the thickness of the coating. The positron implantation profile is usually parameterized by a Makhovian profile giving a mean implantation depth [9] of:

$$\bar{z} = \frac{\alpha}{\rho} E^n \quad (2)$$

where  $\alpha = 4.0 \mu\text{g}/\text{cm}^2$ ,  $n = 1.62$ ,  $\rho$  is the density of the material and  $E$  is the energy of the positrons in keV. The thickness of the layer was accurately determined by the VEPFIT program, resulting in 535 nm (see Table 1). The transition from annihilation of positrons in the polymer to annihilation in the steel

Table 1. Multilayer VEPFIT analysis of IF steel coated with epoxy 1004 and epoxy 828. Diffusion lengths and boundary location are shown. Errors of the fitted values are typically in the order of 10%

Sample	$L_{\text{epoxy}}$ (nm)	$L_{\text{steel}}$ (nm)	$D_{\text{boundary}}$ (nm)
Epoxy 1004	2.4	108	535
Epoxy 828	2.4	124	496

takes place in a broad energy interval due to the straggling of the implantation profile and the long diffusion length of the steel (108 nm, see Table 1). In other words, positrons implanted far from the epoxy layer can end up annihilating on the polymer/steel interface.

So from the  $S(E)$  plot two different layers were characterized: a thin layer of epoxy ( $\sim 500$  nm) and the thick IF steel substrate. Each layer was defined by the fitted  $S_i$ ,  $W_i$  coordinates. Assuming that annihilation occurs only in these two layers, the data points in the  $S$ – $W$  map must lie on a straight line connecting the  $S_i$ ,  $W_i$  cluster points of epoxy and steel. This is due to the linear definition of both parameters. In Fig. 3 such a plot is shown for the epoxy 1004. It can be observed that there is a deviation from linearity, so a third trapping layer has to be included between the other two. This third trapping site is ascribed to the interface between both materials and its study will be crucial in understanding the cohesion of the polymer to the metal.

With the aid of VEPFIT, the data of  $S$ – $W$  measurements were analyzed in terms of three positron trapping layers. The results of this analysis are summarized in Table 2. It shows that the diffusion length of the epoxy layer is very short compared to that of the steel. In the model the interface was assumed to be a perfect sink for positrons. In Fig. 4 the positron energy dependence of the fraction of positrons annihilating in the different layers is shown. It can be seen that even for high implantation energies of 10–15 keV there is still an important fraction of positrons annihilating at the interface. Because of the high diffusion length in the steel, positrons implanted deep in the steel can diffuse back to the interface and become trapped there. One very interesting experiment would be applying an electric field to the samples, drifting the positrons to the interface. That kind of experiment will provide very interesting information about the interface of the coating.

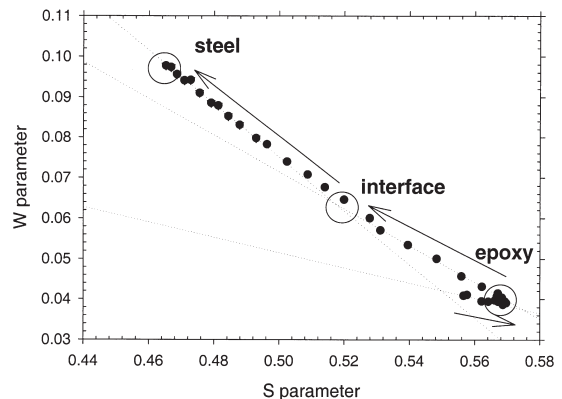


Fig. 3.  $S$ – $W$  map of the IF steel sample coated with epoxy 1004. The dotted lines show linear regressions of the  $(S, W)$  points to determine graphically the positron trapping sites marked by larger circles. Arrows indicate the direction of increasing positron implantation energy.

Table 2. VEPFIT analysis of  $S$ - $W$  parameters for IF steel coated with epoxy 1004 during stretching. Errors affect the last significant digit

Strain (%)	$S_{\text{epoxy}}$	$W_{\text{epoxy}}$	$S_{\text{interface}}$	$W_{\text{interface}}$	$S_{\text{steel}}$	$W_{\text{steel}}$
0	0.5680	0.039	0.517	0.064	0.457	0.107
1	0.5685	0.0385	0.517	0.064	0.457	0.106
10	0.5690	0.0384	0.517	0.064	0.475	0.095
20	0.5700	0.0385	0.518	0.064	0.479	0.093
35	0.5700	0.0384	0.519	0.064	0.484	0.089

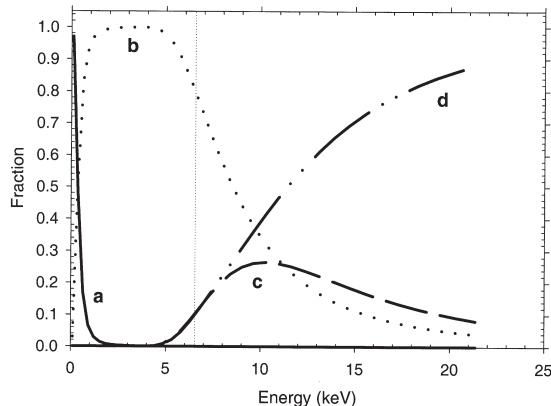


Fig. 4. VEPFIT fitted results of energy dependent fractions of positrons annihilated at: (a) the surface, (b) in the epoxy layer, (c) at the interface, and (d) in the steel substrate for IF steel coated with epoxy 1004 without stretching. The vertically dotted line indicates the location of the interface boundary (535 nm) according to VEPFIT analysis.

The samples of epoxy 1004 were measured again after stretching to different strains levels. The ductility of the IF steel is 43% so strains from 1 to 35% were applied in order to have a wide range of elongations. The behavior previously described for a coated sample before stretching was observed in all the samples after elongation. At least a reduction in the thickness of the layer was expected because of the strain; as in plastic deformation, the volume should be conserved. However, on stretching, although the length increased, the width decreased, creating a “neck”. So the thickness was not affected by the stretching and no differences were found with the positron experiments. An  $S$ - $W$  map with the strain as a running parameter might shed more light on the differences in the coating due to the applied stress. In Fig. 5 such a map is presented. An increase in the  $S$  parameter at the interface would be a sign of decohesion due to the creation of open volume defects. As it turns out, no differences are noticed either at the epoxy layer or at the interface. On the other hand, after 10% elongation, the effect of deforming the steel substrate is observed by the increase in the  $S$  parameter and by the decrease in  $W$ . The epoxy coating seems to follow the surface of the steel perfectly. We conclude that the strain rate was low enough to permit the polymer to rearrange itself at every new situation of the substrate. Further experiments increasing the strain rate will be performed. It

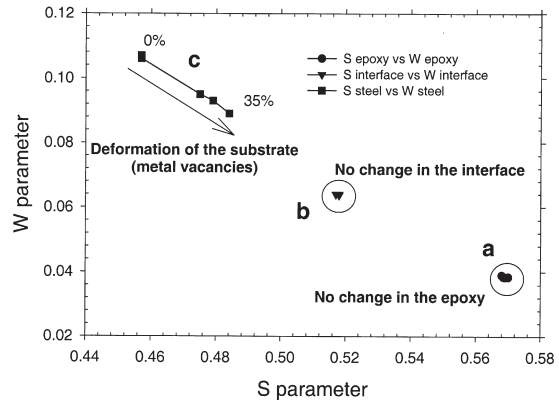


Fig. 5.  $S$ - $W$  map of the IF steel sample coated with epoxy 1004 with the strain as the running parameter. The circles mark the three positron trapping sites: (a) epoxy layer, (b) interface, and (c) steel substrate. The arrow indicates the direction of increasing strain from 0 to 35%.

is known that this kind of polymer is used normally as a primer in coatings so the adhesion to the substrate is excellent. It would be interesting to coat the samples with another type of polymer. When cavities are larger than nanometer size they will be clearly observed by positron beam analysis.

#### 4. CONCLUSIONS:

Doppler broadening of positron annihilation radiation presents some advantages for the study of interfaces and therefore the adhesion of coatings. It is a non-destructive and depth sensitive technique, and also offers some additional features as  $S$ - $W$  plots to trace changes in the system during treatment. In the samples studied no decohesion of the epoxy on the metal after stretching was observed. The technique is sensitive enough to detect small variations in the open volume defects in the material, but no significant difference was measured at the interface. Experiments in which electric fields are applied to drift the positrons to the polymer/metal interface will complete this study in order to obtain a more detailed analysis.

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