JOURNAL OF MATERIALS SCIENCE **39** (2004) 4263–4269

# Positron annihilation studies of the subsurface zones created in the copper under the indium coating

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The positron annihilation spectroscopy has proven to be useful method for the investigation of defects in subsurface zones created e.g., during the sliding contact of two metals or the indentation. The present work is focused on the study of the defect profile which occurs in the copper substrate coated by the indium layer and covered by the indentations with the small ball. In our studies we showed that the coating reduces the extension of the defect depth profile and changes its shape as well. The experimental studies have been correlated with the theoretical predictions in the frame of the elasticity theory. © *2004 Kluwer Academic Publishers*

## 1. Introduction

The topic of this paper is the defect profile which occurred in the copper substrate covered with the indium layer as a result of the Hertz contact. The positron annihilation technique used in the studies is suitable for detection of the open volume defects created in subsurface zones after deformation as it was claimed in our former papers [1–4]. The series of investigations of the subsurface zones created in sliding contact of two metals performed using positron annihilation spectroscopy showed interesting features of the obtained defect profiles. We have also reported results of the studies of the defect profile induced by the static indentation in copper samples [5]. Comparison of the defect profile detected by positron technique with the distribution of the stress calculated theoretically using the relations originated from the elasticity theory has shown that onset of the range of the detected defect profile corresponds with onset of the yield strength. Nevertheless, the defect profile exhibited local maximum and minimum and this is in contradiction to the monotonic decay of the stress depth profile.

In many applications substrate's materials are covered by coatings or paints, for protection or decoration. We think that it would be interesting to find the defect profile in such a case as well. We intend to give an answer to the question how the cover influences the defect depth profile which occurred in the substrate. Is the positron technique suitable for such a study? Our work presents rather preliminary results which should encourage us to do future studies. Nevertheless, it should be noticed that the study of polymer/metal coating using the positron annihilation spectroscopy has been reported [6].

## 2. The experimental details

As a substrate we have used the well annealed copper plate of size 1.5 cm × 1.5 cm and 3 mm thick. The annealing process was performed at 950°C during 24 h in vacuum and then the samples were slowly cooled to the room temperature in order to obtain the virgin samples with residual defects only. The substrate was covered by the indium layer in the electrodeposition process. We used the solute of 0.3 M of $In_3(SiO_4)_2$ and 0.5 M of NaCl in distillated water [7]. Indium was chosen because it a soft, malleable and ductile metal different than copper. In our studies we have used the conventional measurements of the Doppler broadening (DB) of the annihilation line. This is a commonly used experimental technique which is very sensitive to small changes of the defect concentration. We have measured the annihilation line of energy 511 keV using the high-purity germanium (HpGe) detector of energy of resolution FWHM = 1.40 keV at 586 keV. From the measured annihilation line we extracted the so-called S-parameter. It characterizes the shape of the 511 keV positron annihilation line and is defined as the ratio of area of a suitably chosen central part and the total area of the annihilation line [6]. The integration range in the central part of the annihilation line was chosen as follows: (511 ± 1.13 keV). The S-parameter is sensitive to the presence of low momentum electrons annihilating with positrons. Such electrons are present in open volume defects like vacancies and their clusters. Electrons located in the interstitial regions of non-disturbed bulk crystalline lattice exhibit larger momentum which is visible in the positron experiments quite well. This is the physical outline of this technique. With an increasing fraction of positron trapped, e.g., in vacancies, the DB of the annihilation line is reduced and the S-parameter increases. In order to deduce from the DB experiment the type of defects it is convenient to extract from the measured annihilation line also the so-called wing (W) parameter. It is defined in a similar way to the S-parameter however the integration limits are fixed in the region where the annihilation with the high momentum electrons is reflected. For this parameter we have chosen the limits of integration as follows: (516.41–516.94 keV). This parameter is sensitive to the high momentum electrons which are present in the core region of atoms [6]. Change of the shape of the positron wave function localized in an open volume defect induced by the geometry and shape of the defect influences the annihilation with the core electrons. This helps to identify the open volume defect.

It should be also noticed that positrons emitted from the 22-Na source used in our experiments are implanted at a certain depth. In copper 87.4% of positrons penetrate the depth up to 28 $\mu$m. Then during one measurement the value of the S-parameter is integrated over that range. This is the depth resolution of our experimental technique.

## 3. The sample preparation

In the experiment a martensite steel ball 4 mm in diameter was forced in the surface of the copper substrate covered with indium with a normal load equal to 20 N. The whole surface was damaged by the indentations and the distance between these indentations was 1 mm. This was necessary because our radioactive source has a diameter of 1 cm and the positrons illuminated such an area.

The procedure used in our experiment has been presented in Fig. 1. First the indium cover of certain thickness has been put on the copper plate in the electrodeposition process, Fig. 1a. Then the indentation was performed, Fig. 1b. After that the indium layer was removed in the electroetching process, Fig. 1c. The copper samples without indium layer were measured as follows. The kapton's (foil 7 $\mu$m thick foil) envelope with the positron source $^{22}$Na (activity 20 $\mu$Ci) was located on the damaged copper surface and the next identical sample sandwiched the source, Fig. 1d. Then we measured the positron annihilation line using the HpGe detector and extracted the S- and W-parameters. After that the copper samples were etched in nitrogen acid to reduce their total thickness about 40 $\mu$m, it means that from one side only the layer about 20 $\mu$m was removed and the next measurement of the S-and W-parameters was performed. (The accuracy of the measurement of the total thickness of the etched layer was $\pm 5$ $\mu$m.) The sequenced measurement allows us to monitor the depth distribution of the S-parameter which tags the defect distribution in a damaged subsurface zone. One should state once again that we monitor the subsurface zones only in copper samples because the indium layer after the indentation was removed.

## 4. The results for the ball indentation

The ball indentation has been performed for two samples with different thickness of the indium layer, equal

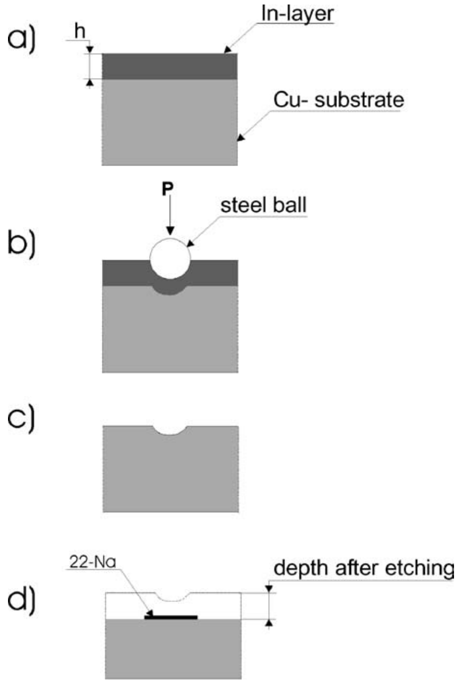

*Figure 1* The scheme of the experiment reported in this paper. First, on the well annealed copper substrate the indium layer in the electrodeposition process was created (a). Then the indentation was performed using the steel ball 4 mm in diameter (b). After that the indium layer was removed in the electroetching process (c). Finally the substrate was etched and subsequently the S-parameter was measured (d).

to 12 and 25 $\mu$m, respectively. Using the ELASTICA program [8] we were able to generate the stress distribution in the substrate and layer. In Fig. 2 we present the contour plot of the von Mises stress defined as

$$\sigma_{\mathrm{M}} = \sqrt{\frac{1}{2}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]},$$

where $\sigma_{1-3}$ are principal stresses. This stress is used as the criterion for yield, i.e., the plastic deformation onset occurs for $\sigma_{\mathrm{M}} = \mathrm{Y}$, where Y is the yield strength—for soft copper equal to 55 MPa. This is called the von Mises criterion for yield. For comparison we present the contour plot for the case without covering indium layer in Fig. 2a and for the layers of thickness 12 and 25 $\mu$m in Fig. 2b and c, respectively. Note, the monotonic nature of the calculated stress field at the depth more than 50 $\mu$m its value decreases with the increase of the depth. It is well visible also that the presence of the indium layer reduces the depth distribution of the stress $\sigma_{\mathrm{M}}$ and changes the shape of the contour. The increase of the layer thickness from 12 to 25 $\mu$m slightly increases the depth profile of the stress. Similar tendency we observed also for the shear stress distribution not presented here. This can be understood in the following way. If the thickness of the indium layer is small the pressing of the ball induces the extrusion of the indium layer and the substrate deeper is less damaged. For the larger thickness of the soft layer the substrate is protected against the pressing which begin to act only on the layer. Using the ELASTICA program we extracted the depth of the onset of the plastic deformation applying the von Mises criterion for yield as the function of the thickness of the indium layer, Fig. 3. The obtained dependency exhibits the maximum at the depth about 60 $\mu$m which separates both mechanisms.

In Fig. 4 we depicted the measured depth profile of the S-parameter for three substrate samples not covered, $h = 0$ and covered before the indentation with the indium layer of thickness equal to 12 and 25 $\mu$m. In the figure we added also the theoretical von Mises ($\sigma_M$) and the maximal shear stress ($\tau_{max}$) distribution direct beneath the ball ($x = 0$). The stress distribution exhibits a maximum close to the surface and monotonically decreases reaching at a certain depth the value

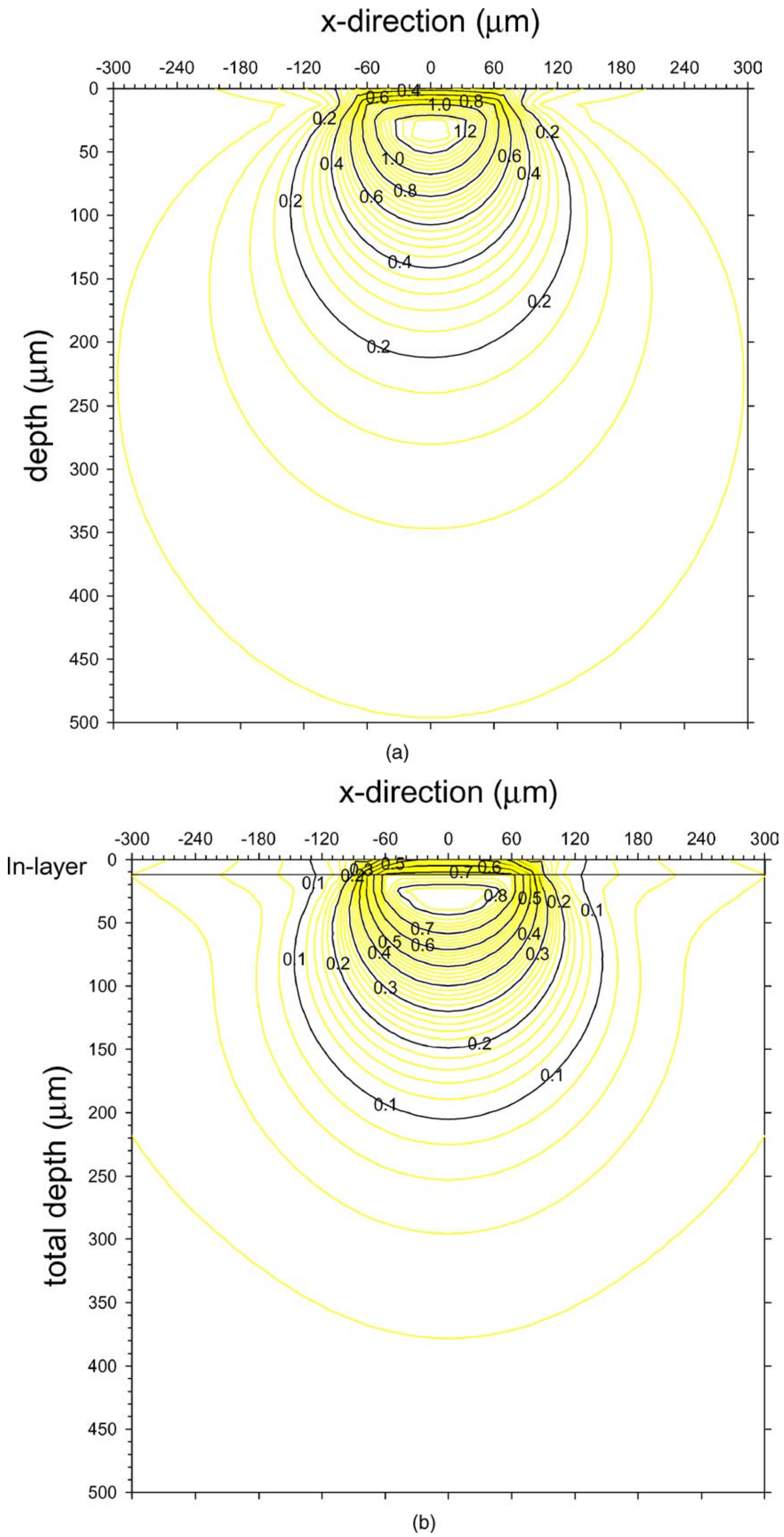

*Figure 2* The contour plot of the von Mises stress distribution in the indium layer and the copper substrate deduced from the elasticity theory. For this the code of the program ELASTICA has been used. The calculations have been performed for the indium layer of thickness 0 (a), 12 $\mu$m (b) and 25 $\mu$m (c). The digits represent the stress value in GPa. (*Continued*)

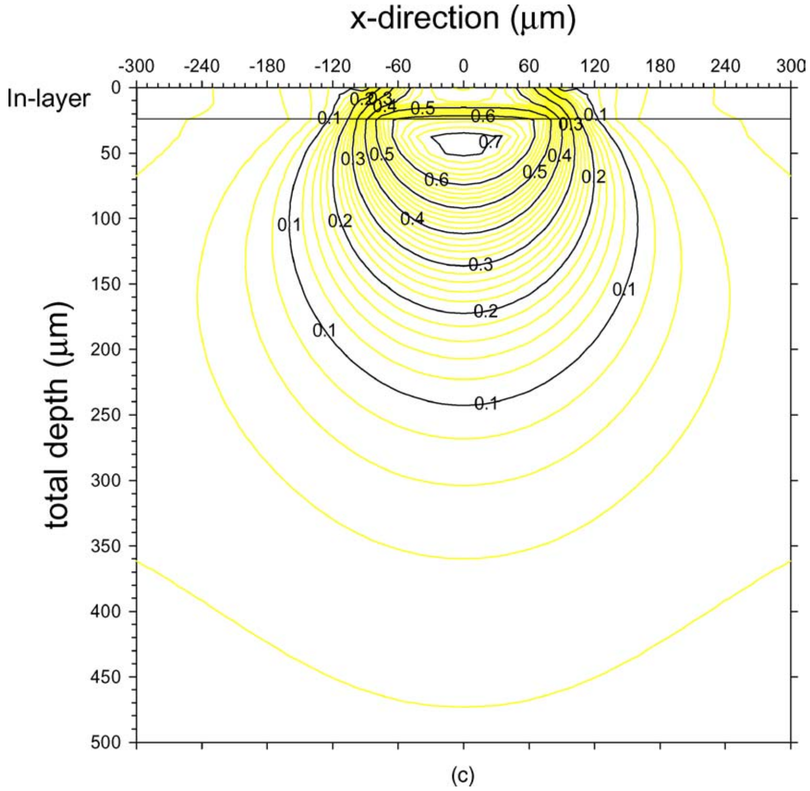

*Figure 2* (*Continued*).

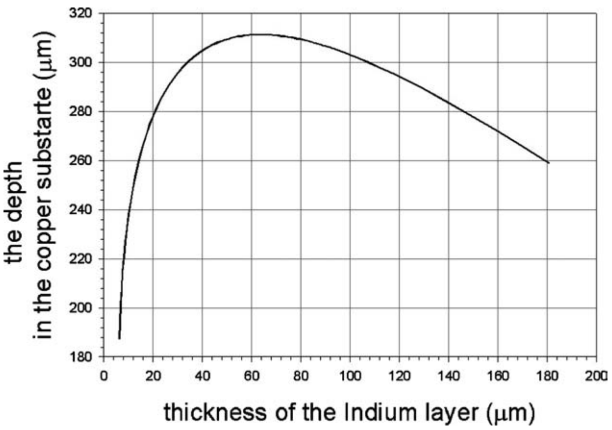

*Figure 3* Dependence of the depth of the onset of the plastic deformation in copper as the function of the thickness of indium layer which covers the copper as the substrate. The values were extracted from the ELASTICA program [8] using the von Mises criterion for yield.

of the yield strength—Y. In Table I we gathered the value of the depth at which the von Mises and shear stress reach the yield strength. We will treat this depth as the theoretical onset of the plastic deformation zone. Certainly, the layer reduces this depth significantly in comparison with the case with no layer covered the copper substrate during the indentation. Note, the latter the depth is equal 420 $\mu$m but when the 12 $\mu$m layer of indium covered the substrate the depth is equal to 249 $\mu$m only. The increase of the thickness of the indium layer up to 25 $\mu$m slightly increases the depth to 286 $\mu$m, Table I.

The measured value of the S-parameter decreases with the increase of the depth but it is not a smooth monotonic function as the stress distribution, Fig. 4. In the case when no layer was present during indentation at the depth about 200 $\mu$m, 280, and 370 $\mu$m it exhibits the local maximum, Fig. 4a. It points out the layer structure of the zone where the defect density changing rapidly. The bulk value of the S-parameter measured for no damaged, well annealed copper substrate is reached at the depth 450 ± 5 $\mu$m and this is the onset of the subsurface zone. Beneath this depth not damaged area is extended. The rapid changes in the value of the S-parameter close to the onset of the subsurface zone are not detected when indium layer covered the substrate. For the sample with the indium layer of thickness 12 $\mu$m the local minimum at the depth 40 $\mu$m is observed only but then the S-parameter is decreasing to the depth 260 ± 5 $\mu$m when the bulk value is reached. For the sample with the 25 $\mu$m thick indium layer, at the depth less than 100 $\mu$m a local minimum and maximum are present and then the value of the S-parameter decreases to the bulk value at the depth 280 ± 5 $\mu$m. The increase of the thickness of the indium layer significantly reduces the value of the S-parameter measured on the surface of the substrate (depth equal to zero) just beneath the indium layer. For the 25 $\mu$m thick layer it is 0.5260 ± 0.0003 and for the 12 $\mu$m it is equal to 0.5288 ± 0.0003. There are no significant differences in the value of the S-parameter on the surface for the sample where $h = 0$ and $h = 12$ $\mu$m. It points out that in this case the concentration of defects beneath the indium layer in the substrate is almost the same like for the substrate not protected by the layer. The increase of the thickness of the indium layer up to 25 $\mu$m siginifcantly reduces the defect concentration. It is well visible from Fig. 4 that the character of the S-parameter dependency on the depth is different if the layer was present during

TABLE I The values of the depth of the onset of the yield strength obtained for two yield criterions depending on the thickness of the indium cover. In the last column the onset of the defect profile determined by the positron annihilation measurements is presented

| Thickness of indium layer ($\mu$m) | Depth from the von Mises yield criterion $\sigma_M = Y$ ($\mu$m) | Depth from the criterion: $\tau_{max} = Y$ ($\mu$m) | Experimentally detected onset of the defect depth profile ($\mu$m) |
|---|---|---|---|
| 0 | 420 | 291 | 450 ± 5 |
| 12 | 249 | 186 | 260 ± 5 |
| 25 | 286 | 206 | 280 ± 5 |

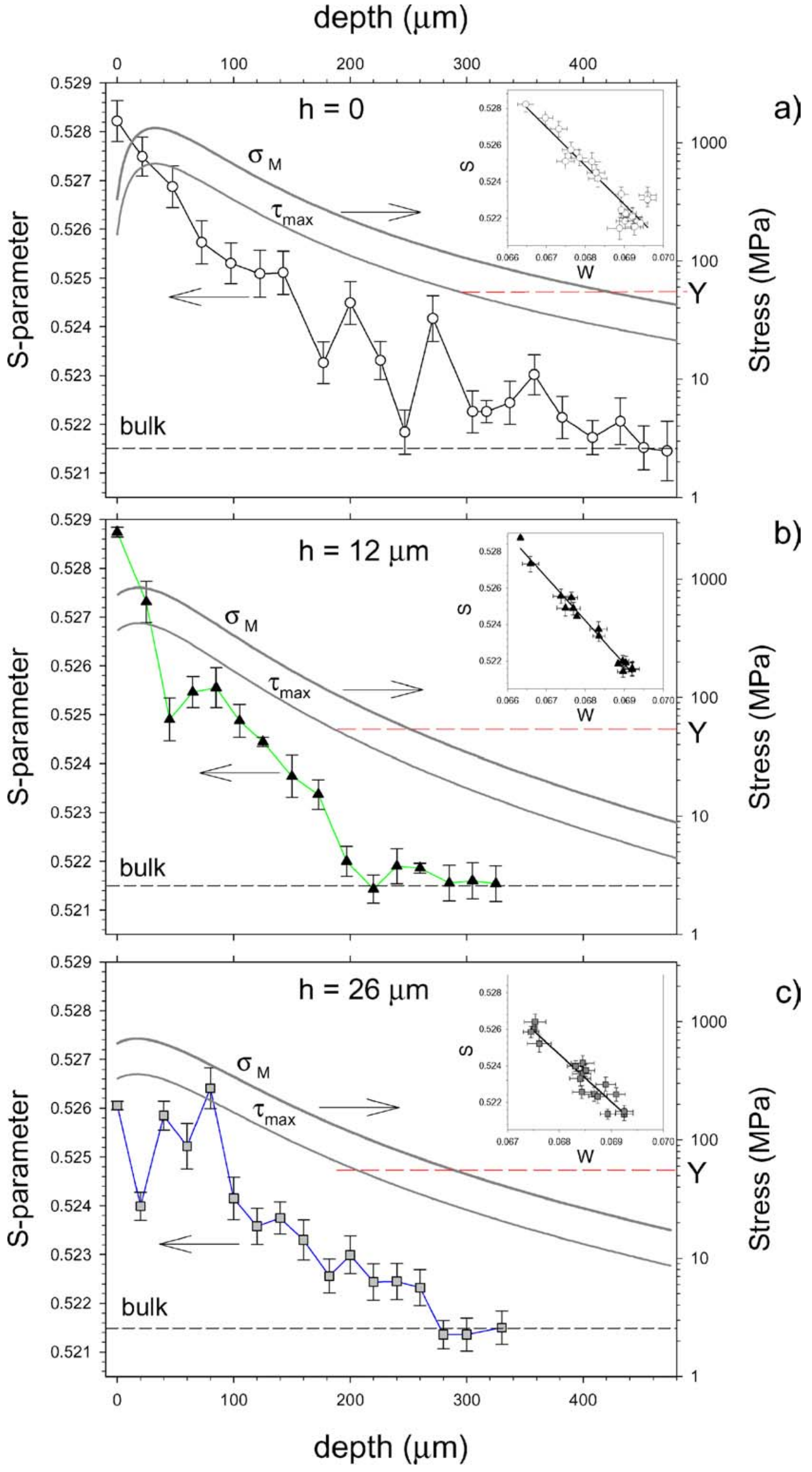

*Figure 4* Dependence of the S-parameter on the depth in the copper substrate whose surface with the indium layer was covered by the indentations of the small ball with the normal load 20 N. The thickness of the indium layer was equal to $h = 12$ $\mu$m (b) and $h = 25$ $\mu$m (c). The values of the S-parameter for the case when no indium layer covered the substrate $h = 0$ were taken from the reference [5]. The solid lines represent the calculated von Mises $\sigma_M$ and $\tau_{max}$ stresses beneath the ball. In the inset we present the dependency of the S-parameter on the W-parameter extracted from the annihilation line.

the indentation. This is not reflected in the theoretical dependencies of the stress distribution.

In the insets of Fig. 4 we present additionally the diagrams of the S-parameter versus the W-parameter. All points are located on the straight lines which suggests that the type of defect in the subsurface zone is not changing. Therefore, the values of the S-parameter in Fig. 4 reflect the change in the defect concentration. The value of the slop for each sample is slightly decreasing, for $h = 0$ it is equal to $-2.11 \pm 0.20$, for $h = 12$ $\mu$m it is equal to $-2.37 \pm 0.10$ and for $h = 25$ $\mu$m it is $-2.58 \pm 0.22$. It suggests that the type of defects is changing with the increase of the thickness of the indium layer.

We can drawn the conclusion that the indium layer reduces the total depth profile due to the reduction of the yield range but only for the higher thickness the significant reduction of the defect concentration is observed. It is interesting to confirm once again that the onset of the defect profile detected using positron annihilation method is well correlated with the von Mises criterion for the yield. In Table I we give also the depth at which another criterion i.e., $\tau_{\max} = Y$ is fulfilled. Unfortunately for this case the depth is much lower than this observed experimentally in the S-parameter measurements.

## 5. The results for the blasting experiment

In our previous studies we have found that blasting process of the surface of the copper samples using the small hard particles induced the smooth depth profile which is similar to the depth profile detected when the surface was damaged during the sliding process of the steel ball on the copper samples. It points out that the mechanism of creation of the defects during blasting process when small particles bomb the surface and during the sliding can be similar and different than in the indentation. In the first cases the processes are dynamic and chaotic but in the latter it is static and well defined.

As above the copper well annealed substrate covered before with the indium layer were blasted by silicon carbide particles with a pressure of 6.5 bar [5]. After that, the indium layer was removed from the surface. Microscopic observation has shown no silicon carbides particle on the copper surface and the depth profile of the S-parameter was measured in the similar way as above. We have noticed that the layer of thickness 25 $\mu$m was almost destroyed and partly removed during this process and the silicon carbide particles had the opportunity to hit the surface of the copper. Indeed the depth profile of the S-parameter for this sample differs only slightly from the depth profile when the blasted surface was not covered by indium layer, $h = 0$, Fig. 5. Only on the surface the value of the S-parameter is reduced but the total depth is similar. But the increase of the indium thickness up to 36 $\mu$m, causes the significant change in the depth profile of the S-parameter. The total depth is reduced from almost $280 \pm 5$ $\mu$m for $h = 25$ $\mu$m to 60 $\mu$m for $h = 36$ $\mu$m. The value of the S-parameter close the surface is also reduced. It indicates that the lower number of defects was created in this case and the layer of thickness 36 $\mu$m in a significant way protect the substrate against the defect creation. Nevertheless, some defect profile occurred as well. During blasting process the type of defect is not changing. It is well visible in the right part of the Fig. 5 where the dependency the S-parameter on the W-parameter is depicted. The slop for this dependency is equal to $-2.72 \pm 0.10$ and it is different than obtained in the indentation experiment. From this we can conclude that different type of

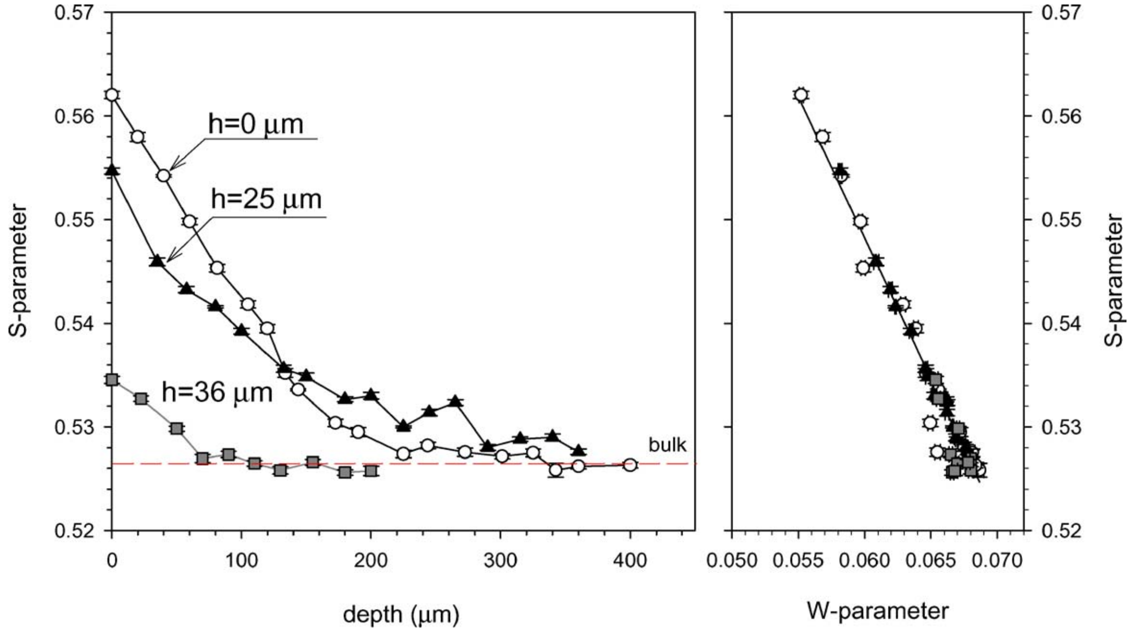

*Figure 5* Dependency of the S-parameter on the depth of the copper sample whose surface covered by the indium layer was blasted with the small silicon carbide particles with the pressure 6.5 bar. The thickness of the layer was marked in the figure. The values of the S-parameter for the case when no indium layer covered the substrate were taken from the reference [5]. On the right the S-parameter versus the W-parameter extracted from the annihilation line.

defect is created during the blasting experiment than in the indentation.

## 6. Conclusions

We can conclude that in the positron annihilation experiment we were able to distinguish the difference in the subsurface zones created under the protected layer. There was detected the reduction of the onset depth of the subsurface zone when the indium layer protected the surface of the copper substrate in the ball indentation and when the sample was blasted. The observed changes followed the von Mises stress criterion. Nevertheless, the observed defect profile in the substrate exhibited the layered structure and this is in contradiction to the theoretical results of the stress distribution in the subsurface zones.

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*Received 30 October 2002*
*and accepted 18 March 2004*