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Slow positron annihilation studies of vacancy-type defects in the near-surface region of Cu and Nb before and after wear

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Abstract. The distribution of the vacancy-type defects in the near-surface region of single-crystalline Cu and Nb before and after wear was investigated by slow positron annihilation. It was found that a lot of vacancy-type defects were produced by wear in Cu samples. For Nb, the S parameters in the area from the surface to the depth of 160 nm after wear were smaller than both those in the same area before wear and those in the area beyond 320 nm after wear, which was possibly due to the resulting compounds, new phases, or different types of defects in the very near surface region. In the depth beyond 320 nm, the S parameter profile of Nb after wear shows that in this area a lot of vacancy-type defects were produced by wear.

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The positron annihilation technique has been widely used to study the vacancy defects in semiconductors [1], various thin films, and interfaces [2, 3] during recent years. Positrons are localized in the attractive potential of vacancies and this trapping is indicated by a distinct change in the annihilation parameters [4]. Positrons are very sensitive to the atomic-size defects, especially vacancy-type defects, such as vacancies, vacancy clusters, dislocations, etc. The positron annihilation technique can measure defect concentrations as low as 10^{-7} [5]. However, the technique as a powerful defect detector had not been applied in the field of wear and friction until Dryzek et al. [6] utilized this method to investigate the dependence of the defect distribution behavior on the wear load, duration, etc.

It is well known that the density and distribution of the defects induced by wear or friction in the material near-surface region (less than several µm) play very important roles in understanding the wear mechanism. The positron penetration depth into the solid materials is about several hundred µm because the energy of a positron directly obtained from β nuclear decay is about 0.5 MeV to 1.5 MeV depending on different nuclear sources. This makes this kind of positrons not suited for studying the defects in the near-surface region. In this paper, the slow positron technique was used to investigate the distribution of the vacancy-type defects in the near-surface region of single-crystalline Cu and Nb before and after wear. With a monochromatic positron beam, the slow positrons can be implanted at a fixed depth beneath the material surface and the vacancy-type defect distribution with various depths in the near-surface region can be obtained by changing the positron energy from 0 to 18 keV.

1 Experimental procedures

To reduce the inherent defects in the sample near-surface region to a level as low as possible, the single crystals of Cu and Nb (purity 99.9%) with a size of 16 mm × 16 mm × 1.5 mm were selected as test samples and were treated according to the following procedures. The samples were polished to a perfect mirror surface by mechanical method. Then an electrolysis polishing method was used to eliminate the defects induced by mechanical polishing. The crystal faces of Cu(111) and Nb(111) were parallel to the polished surface. To further reduce the defects, the samples were annealed in a vacuum annealing furnace at temperatures of 200 °C and 800 °C for 0.5 h for Cu and Nb, respectively. The cooling process was furnace-cooled. The vacuum during the annealing and cooling process was kept at $1–2 \times 10^{-5}$ Torr.

The wear tests were carried out on an RFT-III reciprocating wear tester. The sample was mounted on the upper sample holder and pressed horizontally onto the canvas surface, which can move back and forth relative to the sampler holder. Table 1 shows the wear parameters of the Cu and Nb. To minimize surface contamination because of annealing and wear, all samples were cleaned with methanol in an ultrasonic cleaner.

The samples before and after wear were subjected to the slow positron measurement with the positron beam facility at the University of Science and Technology China, Hefei, People's Republic of China [7]. The positron moderator is W. The energy of the slow positron beam can be changed from 0

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Table 1. The wear parameters of the Cu and Nb samples

Sample	No.	Load /N	Repetition rate /min^{-1}	Travel distance /mm	Wear time /min
	1		before wear		
Cu	2	490	50	50	100
	3	245	50	50	100
	1		before wear		
Nb	2	784	50	50	100
	3	490	50	50	100

to 18 keV and the energy dispersion of the slow positron beam (FWHM) is less than 2 eV. The sample was put into a vacuum sample chamber (1×10^{-8} Torr) for measurement. A high-purity Ge detector was placed behind the sample chamber to detect the 511 keV energy spectrum of the annihilation photons. The total counts of the spectrum is 1×10^5.

2 Results and discussion

The Doppler broadening of the 511 keV energy spectrum of the annihilation photons has been characterized by the S parameter [8], which is defined as the ratio of the number of counts under the fixed central channels to the total number of counts under the energy spectrum of the annihilation photons (1×10^5). In our calculation, the fixed central channels were set between 510 keV to 512 keV. The S parameter tends to increase if the momentum of the electrons, with which positrons annihilate, tends to decrease. The fact that the positrons are trapped in vacancy-type defects, where they are more likely to annihilate with lower momentum valence electrons, leads to an increase of the S parameter.

The penetration depth R_p of the slow positron beam into materials is a function of positron energy (E in keV), as shown in the following equation [9]:

$$R_p = AE^n/\rho$$

where ρ is the density of the material, A and n are about 40 (nm g cm^{-3} keV$^{-1.6}$) and 1.6 for most of the materials, respectively. The different R_p can be obtained based on the above equation and the specific materials.

Figures 1 and 2 show the S parameters as a function of the positron energy for the Cu and Nb samples before and after wear, respectively. The corresponding R_p is also shown in the

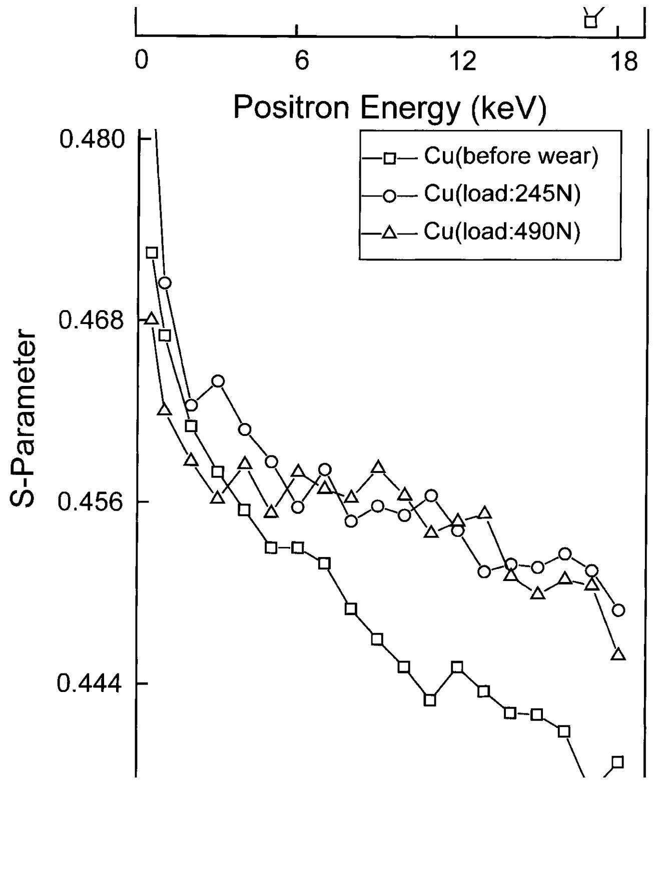

Fig. 1. The variation of S parameter with positron energy for Cu samples before and after wear

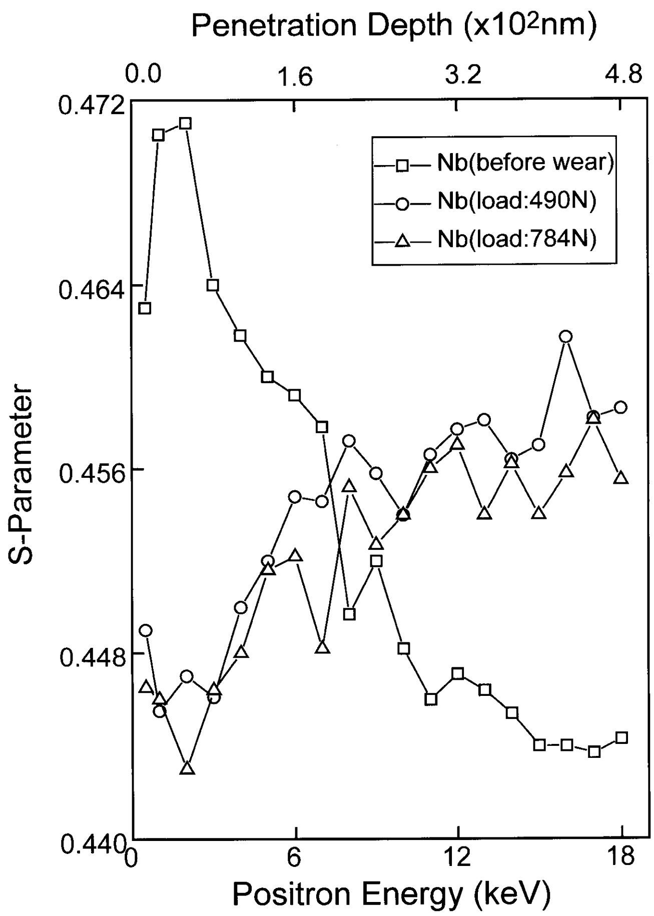

Fig. 2. The variation of S parameter with positron energy for Nb samples before and after wear

figures. The maximum penetration depths are 4.5×10^2 nm and 4.8×10^2 nm for Cu and Nb, respectively.

There are at least three different subsurface zones in the material after wear [10, 11]. The first zone represents the original specimen material in an undisturbed state. Above the first zone, the second zone has a new structure and properties due to tribocontact. That zone contains plastically deformed grains with voids and possibly cracks. On the top, the third zone is a tribolayer, which forms in situ and is very finely structured. Dryzek et al. [11] reported that only the third zone, which is uniform with high defect concentration, could be observed using the slow positron annihilation technique with the maximum positron energy of 25 keV. That means the S parameter should be same at different depths in this zone.

From our results, the S parameters of the Cu sample before wear and the Cu samples after wear decrease with the increase of the positron energy. A similar result was also reported by Dryzek et al. [11]. The reason is that some positrons do not annihilate at the location where they reach, but diffuse back to the material surface and annihilate at the surface area. The percentage of the positrons diffusing back to the material surface decreases with the increase of the R_p. This back-diffusing effect results in the decrease of the S parameters with increasing energy in the Cu samples. For E between 0 to 4 keV, there is no obvious difference among the S parameters of the three Cu samples. This phenomenon can be explained in the following way. When the diffusion distance of the positrons is larger than the R_p, most of the positrons will diffuse back to the material's surface, because the defects induced by wear are negligible when the defects are compared with the surface defects. The "surface annihilation" gives rise to identical S parameters in the region with the depth less than the positron diffusion distance (i.e. less than 100 nm). The S parameters of the Cu samples after wear are larger than those of the Cu samples before wear when E is larger than 4 keV ($R_p > 100$ nm). This result indicates that there are a lot of vacancy-type defects induced by the wear in this region.

Contrary to the reported result [11], there is also no evident difference between the S parameters of two Cu samples after wear under different loads. This probably results from the corresponding pressures, i.e. $1.96\ \mathrm{N/mm^2}$ and $0.98\ \mathrm{N/mm^2}$ for the loads of 490 N and 245 N, respectively, which are much lower than the yield point ($117.6\ \mathrm{N/mm^2}$) of Cu at room temperature and the wear over the canvas surface.

For the S parameters of Nb samples, the S parameter profile of Nb sample before wear is similar to that of Cu sample, but abnormal S parameter profiles of Nb samples after wear under different loads are obtained. The S parameters of Nb samples in the region from the depth of 0 to 160 nm after wear are not only smaller than those of the Nb sample before wear in the same region, but also smaller than those of Nb samples after wear in the area beyond 320 nm. The possible reason for this abnormal result is that the compounds, new phases, or different types of traps (dislocations, voids etc.), whose annihilation characteristic is different to that of Nb, are produced in the very near surface region (less than 160 nm) because of the thermal and stress effects during the wear process. Further investigation is needed here to verify this suggestion. For the region beyond 320 nm, the S parameters of Nb samples after wear are larger than those of Nb samples before wear because many vacancy-type defects are induced by wear in that region. In the region from 160 nm to 320 nm, because this region is located at the transition area from the surface region (0–160 nm) with "low S-parameter materials" to the area with high density of vacancy-type defects (beyond 320 nm) induced by wear, the S parameters of Nb samples after wear in this region increase with the increasing of the penetration depth. The reason why there is no obvious difference between the S parameters of Nb samples after wear under different loads is similar to that of Cu.

The maximum positron energy in this slow positron system is 18 keV. The maximum penetration depth is far away from the boundary of the deformation layer induced by wear for Cu and Nb [6]. So the expected phenomena, that the S parameters of Cu or Nb samples before wear and those of Cu or Nb samples after wear tend to be the same and keep at the constant values with the increasing depth, will occur at the deeper regions and can not be observed by this slow positron system.

3 Conclusions

The following conclusions can be drawn from this research work:

1. It is feasible to investigate the vacancy-type defect distribution in the near-surface region induced by wear by slow positron technique.
2. For single-crystalline Cu, a lot of defects were induced by wear.
3. For single-crystalline Nb, possible compounds, new phases, or different types of defects resulting from thermal and stress effects during wear process make the S parameters of Nb after wear smaller than that of Nb before wear in the very near surface region.
4. For single-crystalline Nb, a lot of vacancy-type defects induced by wear can be detected at the depth beyond 320 nm.

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