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Near surface stress determination in Kr-implanted polycrystalline titanium by the X-ray $\sin^2 \Psi$-method

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Abstract

Ion implantation has been performed on polycrystalline titanium samples with 180 keV Kr^+ ions at various doses from 1×10^{15} to 5×10^{16} ions cm^{-2} at room temperature. The samples where characterised by Rutherford backscattering spectrometry, positron annihilation lifetime spectroscopy and X-ray diffraction. By means of the $\sin^2\Psi$ technique the near surface stress has been determined for both unimplanted and implanted samples. The initial stress state has been shown to be strongly tensile in the first 75 nm below the surface, and weakly compressive deeper inside. The main effect of the implantation process was to relax the pre-existing tensile stress in the track region. An additional compressive stress was introduced deeper in the sample and could be attributed to the presence of larger defect clusters.

Keywords: Titanium; Krypton; Residual stress; Implantation damage; Stress induced diffusion; Stress relaxation

1. Introduction

Ion beam modification of surfaces is generally a complex, non-equilibrium thermodynamic process involving both changes of the strain, microstructure and composition in the near surface region [1]. Implantation causes the introduction of foreign atoms and non-equilibrium defects, whose presence results in local changes of the strain, but the dynamics of which are in turn affected by the presence of stress gradients [2]. Similar effects occur in many fields, including other radiation damage processes, such as neutron irradiation [1], as well as corrosion type processes, such as hydrogen embrittlement [3] and electromigration of thermally generated defects [4]. The aim of this work is to contribute to a better understanding of the mutual interaction between strain fields and point defects introduced in ion implantation processes.

Specifically in this paper, we focus on the effects of the implantation process, and the introduced effects, on the residual stress in the near surface region of a defined specimen. In general the effect of ion implantation on the residual stress has a complicated dependence on dose (fluence), dose rate (flux), implantation energy, implanted species, target material, temperature, and pre-existing stress. For low dose implantation the effect is generally to relax the existing stress [5–8]. For example in polycrystalline titanium argon implantation has been shown to reduce both a pre-existing tensile stress [5] and a pre-existing compressive stress [6]. Various mechanisms have been proposed for this stress relaxation, including plastic flow [8] and defect annealing mechanisms [7]. At higher doses an additional stress is generated in the material which is also associated with radiation hardening effects and an increase in stiffness [9,10]. Generally, the introduced stress is compressive [11,12,7], although an increase in tensile stress has been observed in plasma irradiated stainless steel [13]. The increase in compressive stress is generally thought to occur because of atomic peening effects [7], but changes in the defect and

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microstructure as well as phase transitions at high doses [11] also play a role. For implantation in silicon with a very low pre-existing stress state an introduced compressive stress has also been observed for low dose implantation [10].

The work presented here concerns the effect of the total does of krypton ions on the pre-existing stress state in titanium. The stress is determined using standard X-ray diffraction techniques in samples before and after implantation at different doses. The implanted ion distribution is determined using Rutherford backscattering spectroscopy, and compared with a model profile obtained using the TRIM package [14]. Open volume defects are monitored using variable energy positron annihilation lifetime spectroscopy. After the discussion of the initial stress state, changes in the stresses are correlated with the depth distribution of the implanted ions and radiation damage.

2. Experimental

Disks with a diameter 25 mm and a thickness of 0.33 mm, cut out from a rolled titanium sheet of 99.6% purity, where implanted with 180 keV Kr^+ to total doses of 1×10^{15}, 5×10^{15}, 1×10^{16}, 5×10^{16} ions cm^{-2}. The dose rate was 10^{13} Kr^+/cm^2 s with a beam current of 1.3 μA. Implantation was performed at the Schonland Centre for Research and Nuclear Sciences at the University of the Witwatersrand, South Africa.

Rutherford backscattering spectrometry (RBS), to determine the implanted krypton depth profile, was performed using the single ended Van de Graff accelerator at iThemba LABS, Faure, South Africa. A 2 MeV helium ion beam, at a current of 35 nA and total charge 10 μC, was incident on the sample at an angle of 15°, and the energy spectra of the scattered radiation were recorded using a surface barrier detector at a constant scattering angle of 170°. Under these conditions, the maximum depth probed in titanium is approximately 100 nm, and the minimum energy losses for scattering of the helium beam of titanium and krypton ions are 0.566 MeV and 0.345 MeV, respectively. The krypton, being heavier and concentrated in the near surface region, should therefore appear as a peak to the right of the main, continuous, titanium spectrum.

The beam based positron annihilation lifetime spectroscopy (PALS) was performed using the pulsed low energy positron system (PLEPS) [15] at the Universität der Bundeswehr, München. In this system, the timing information is provided by superimposing a time structure onto the beam using a series of RF bunchers and choppers. The annihilation of the positrons is detected with a BaF_2 scintillator behind the sample. Typically a resolution of 230 ps is obtained at a count rate in excess of 500 Hz.

The probabilistic nature of the annihilation process allows the measured spectrum to be described as a superposition of exponential decay curves from different populations n_i [16],

$$\frac{dN}{dt} = \sum_i \lambda_i n_i(t) = \sum_i I_i \lambda_i e^{-\lambda_i t}, \tag{1}$$

each with an intensity I_i, a characteristic rate constant λ_i, which is usually expressed in terms of its inverse, the lifetime τ_i, corresponding to annihilation from different final states in the solid. The annihilation rates depend primarily on the local electron density sampled by the positron, which is generally reduced for a positron trapped at an open volume defect. The characteristic lifetime is therefore typically 50% longer for a vacancy like defect, than for the corresponding bulk metal. In addition, trapping to defects causes faster depletion of the delocalised state, leading to a first, free lifetime component, which is shorter than the bulk lifetime. In many cases, e.g., when it is not possible to fully resolve different components accurately, the mean lifetime

$$\overline{\tau} = \sum_i I_i \tau_i \tag{2}$$

gives a useful indication of relative changes in the state of the material. In the PLEPS, addition depth information is obtained by varying the incident energy of the beam, and thus the penetration of the positrons into the sample. In this experiment, the maximum energy of 18 keV corresponds to a mean depth of 1.1 μm in titanium.

In X-ray based stress determination the relative change in strain is measured for one set of lattice planes d in different directions in space. This is achieved by tilting the sample normal through an angle Ψ relative to the scattering vector and rotating the sample through different azimuth angles Φ about the sample normal. Assuming a bi-axial stress state the observed strain is obtained by using Hooke's law and a coordinate transformation from the measurement system to the sample frame of reference,

$$\varepsilon_{\Phi\Psi} = \frac{1}{2} s_2 \sigma_\Phi \sin^2\Psi + s_1(\sigma_{11} + \sigma_{22}) \tag{3}$$

where s_1 and s_2 are the X-ray elastic constants for a given reflection, and $\sigma_\Phi = \sigma_{11}\ \cos^2\Phi + \sigma_{22}\sin^2\Phi + \sigma_{12}\ \sin^2\Phi$ is an effective stress which can be expressed as a scalar quantity [17]. For isotropic materials, in general, as a first approximation the X-ray elastic constants can be approximated by the macroscopic Lamé elastic constants, in which case 1/2 s_2 is replaced by the bi-axial modulus $E/(1+\nu)$. This approximation was used in this work using the well accepted values of 11 GPa for Young's modulus E and 0.36 for Poison's ration ν. Eq. (1) shows that $\varepsilon_{\Psi\Phi}$ is a linear function of $\sin^2\Psi$, with a slope which is proportional to the magnitude of the bi-axial stress. This is only true if the stress state is constant over the depth probed by the X-rays. The strain measurements were carried out with a Bruker D8 Advance diffractometer using filtered CuKα radiation at 40 mA and 40 kV. Four different reflections were used, (101) at a Bragg angle of 20.1°, (102) at 26.5°, (103) at 35.4°, and (213) at 69.7°, respectively. The sample was tilted in side inclination mode, perpendicular to the scattering plane, at 10° intervals up to 70° ($\sin^2\Psi$=0.883), and 75°, 80°, 82°, 84°, 86°, 88°, 89° ($\sin^2\Psi$=0.999). At high values of Ψ, the beam is nearly parallel to the surface and so does not penetrate deeply, allowing very near surface stresses to be probed. Conversely at low Ψ the whole region up to the maximum penetration depth is probed. Preliminary studies had shown that the sample is isotropic in the