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Surface modification of metals by ion implantation

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Summary.

The resistance of metals to wear and corrosion is affected by the properties of the surface. In recent years ion implantation has emerged as a new technique to improve these properties by the injection of foreign atoms, often referred to as surface alloying. Ion implantation has marked advantages, in particular a low process temperature, over existing surface treatments like thermal nitriding and the deposition of protective coatings. However, the acceptance of ion implantation as an industrial tool for treating metal tools and components is still rather limited. This is largely due to a lack of control over the properties of the modified layer. A better control requires more basic insight in how the many process parameters affect the microstructure of the implanted surface. These parameters include the type of ion species and target material, the energy and dose of implanted ions as well as the temperature of the target.

The work described in this thesis focusses on the variation with depth under the surface of the microstructural changes, especially the lattice damage, induced by implantation. Up till now this point has received only little attention. Most of the existing depth selective, or depth resolved, studies on implanted metals have been restricted to the depth distribution of the implanted ions.

For our purpose we have developed a technique to prepare cross-section specimens of the implanted surface for investigation in the transmission electron microscope (TEM). These enable a direct observation of the entire modified layer. This XTEM technique has been combined with other methods to obtain information as a function of depth. These techniques, described in chapter 3, include depth selective Mössbauer spectroscopy, RBS/Channeling as well as the modelling of the implantation process by computer simulation.

Chapter 4 deals with implantations in copper single crystals, which serve as a well defined model system. The modified layer appears to be much thicker than the calculated penetration depth of the ions as given by the commonly applied LSS theory. The extension of this deep implantation damage is strongly dependent on the crystallographic orientation of the ion beam relative to the target. The damage depth increases with increasing transparency of the surface, i.e the existence of open channels along atomic axes and planes perpendicular to the surface. From these observations, confirmed by computer simulation, it is concluded that the thickness of the modified layer is determined by the maximum penetration of a small fraction of ions which travel along the open crystal axes and planes. These channeled ions lose their energy mainly to the target electrons because the elastic energy losses due to collisions with the target atoms are largely reduced. This phenomenon of ion channeling is not accounted for by the LSS theory because it assumes the target to be amorphous.

If the copper target is heated to about 400°C during implantation large facetted voids are formed by the coalescence of vacancies generated in the collision cascades.

The injection of extra atoms in the surface layer gives rise to compressive stresses. These stresses are extremely large for the implantation of noble gases, which are insoluble and form bubbles. The high strain fields around these bubbles are the origin of a plastic deformation of the top layer, which is tilted with respect to the bulk material. The low angle grain boundary formed below the surface might be effective in inhibiting fatigue crack initiation by blocking the surface penetration of slip bands originating in the bulk.

The microstructural changes of ion implanted austenitic stainlesss steels are discussed in chapter 5, where various noble gases as well as nitrogen have been chosen as the implanted species. For the noble gas implants the depth extension of the implantation damage is found to be given by the maximum penetration of channeled ions. Gas bubbles are observed at depths corresponding to the calculated penetration of the ions. These bubbles are highly pressurized and contain noble gas which is crystalline and epitaxially aligned with the metal matrix. The pressure is measured to be several GPa and its magnitude seems to correspond well with the thermal equilibrium pressure determined by the surface tension of the metal. On increasing the dose the density of the noble gas inclusions increases and a martensitic transformation is nucleated in the surface layer. The transformation is driven by the high levels of shear stresses around the gas inclusions. Conventionally this transformation is induced by cold working and it is used to harden this kind of steels. As higher stress levels build up during implantation the stress relief from the surface region drives the transformation to larger depths. The transformation efficiency is found to decrease with increasing beam current density, which determines the temperature of the surface region. The transformation is also strongly dependent on the precise composition of the steel, i.e the chromium and nickel content, which determines its austenite stability.

The implantation of nitrogen, which has been reported to have very beneficial effects on wear resistance, has been studied with particular emphasis on the possible formation of martensite, as has been claimed by several investigators. We found no traces of martensite up to very high doses, although the pressure in the surface region, due to the oversaturation with nitrogen, is sufficient to create blisters at the surface.