Radiation Enhanced Titanium Segregation and Oxide Formation in NiTi

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Metallic implants, even those made out of light titanium alloys, still show a different elastic behaviour than biological bone material. Super-elastic shape memory alloys as NiTi are much more adapted for use in natural surroundings so that a much better biocompatibility and faster healing of bone fractures can be expected. However, the high nickel content may constitute a problem as release of Ni ions can lead to allergies or other complications.

In the present experiment, plasma immersion ion implantation (PIII), where positive ions are accelerated from a plasma by applying negative high voltage pulses on the substrate, was used for implantation of oxygen into a NiTi alloy. Subsequent ERDA measurements were performed with the position sensitive ionization chamber in the ERDA beam line using 200 or 210 MeV Au ions.

Commercial SE 508 (50.8 at.% Ti and 49.2 at.% Ni) was used as a base material. Before oxygen PIII, a thin native oxide layer was removed using Ar ion sputtering at 5 kV for an incident dose of $6 \times 10^{17} O/cm^2$. The remaining oxygen content of the base material is below 0.08 at.%. The temperature and dose range of the subsequent oxygen implantations was 250 - 550 °C and 0.7 - 1.4 $\times 10^{18}$ O/cm^2, respectively.

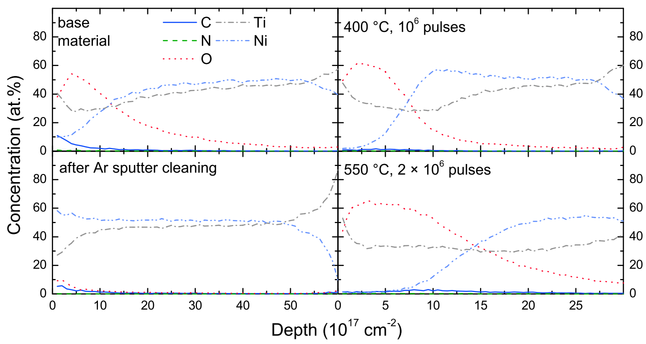

Fig. 1: Atomic depth profiles for differently treated NiTi samples.

The native oxide layer is characterised by an increased titanium and reduced nickel content, together with some carbon contamination (see Fig. 1). After Ar sputter cleaning, the oxygen layer is completely removed. At the same time, the Ni depletion is converted into a slight enrichment in the probed region. The following oxygen implantation leads to a picture similar to the native oxide, albeit with some crucial and significant differences:

At 400 °C and 106 pulses, i.e. 0.7 $\times 10^{18}$ O/cm^2, a thicker oxide layer and a much sharper interface is observed. The actual interface thickness is very small compared to the depth resolution as the measured value is close to that of the experiment. At the same time, more Ni is redistributed from the surface towards the zone below the oxygen implantation with a Ni/Ti ratio of up to 2:1 - or 3:1 if the remaining oxygen is assumed to be present as TiO_2. Increasing the temperature and dose leads to a further change with the oxygen distribution becoming broader, both in the width of the plateau and the diffusion tail, with the latter extending beyond the accessible depth range. Integrated concentration measurements show no preferential sputtering of either Ti or Ni at the surface, instead all the Ni is found to agglomerate below the surface. The transport seems to be mainly by mobile oxygen atoms, pushing the Ni inwards by irradiation and chemical effects [1].

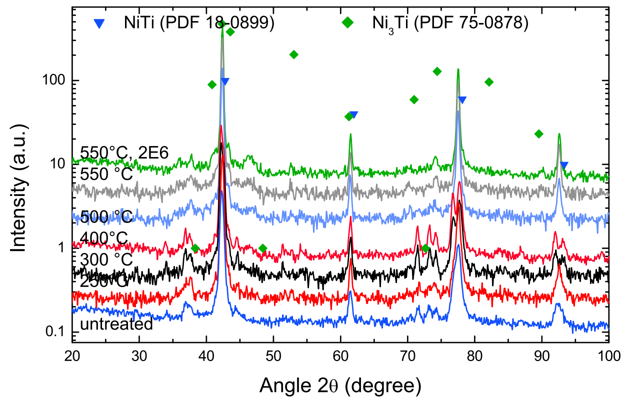

Fig. 2: X-ray spectra for NiTi implanted with oxygen at different temperatures.

Parallel to the elemental depth profiles, phase analyses were performed using X-ray diffraction. The surface rutile layer itself is barely visible in the spectra due to the very small grain size of 10 - 30 nm. However, additional strong reflections were found beside the austenitic NiTi base material, which could be identified as Ni_3Ti (see Fig. 2).

The diffraction intensity is most pronounced between 300 and 400 °C. At low temperatures, the atomic mobility was too low to allow the formation of large crystallite. In contrast, at higher temperatures the mobility is significantly increased, thus the radiation induced segregation is reversed by thermal processes and the local Ni concentration is not sufficient to trigger the formation of Ni_3Ti precipitates below the titanium oxide surface layer.

Animal test with dogs were performed in conjunction with the investigation on the diffusion and phase formation. A highly improved biocompatibility and a significantly reduced tissue response was found for the samples implanted at 400 °C. This indicates that the surface segregation, the sharp interface towards the bulk and the trapping of Ni in large stable Ni_3Ti crystallites are decisive factors for lowering the outdiffusion rate and improving the biocompatibility.

References

[1] S. Mändl *et al.* 13th Int. Conf. on Surface Modification of Materials by Ion Beams, San Antonio, Texas, (21. - 26. 9. 2003)