

Radiation Modified Oxide Growth in the System Ni-Ti-O

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Recently, medical products based on NiTi have experienced an exponential growth, driven by advanced manufacturing techniques and the use of progressively less invasive medical procedures. A thin native oxide layer of about 1 nm is usually present at the NiTi surface, which leads to a high surface energy and a hydrophilic surface. However, the load bearing capability of this oxide is very limited, thus extensive loading/unloading cycles with a corresponding mechanical attrition are to be avoided. Therefore, several strategies to improve the bio-compatibility of NiTi have been developed. One possibility, well-established on the laboratory scale, is the formation of a thick protective oxide layer on NiTi by plasma immersion ion implantation (PIII). By oxygen ion implantation at elevated temperatures, a surface region of TiO₂, devoid of Ni, followed by a Ni₃Ti layer in the deeper interface region is obtained [1]. Beside selective sputtering of Ni, a diffusion of Ni cations towards the bulk is responsible for this effect. During isotope marker experiments to elucidate this effect, it was noticed that the growth of the oxide layer was influenced by the marker ion implantation, i.e. higher marker fluences lead to thinner oxide layers [2]. Here, the influence of the energy loss mechanism, nuclear or electronic energy deposition, during the pretreatment and the temperature of the subsequent oxygen PIII is investigated [3]. Polished NiTi plates of grade SE-508 were used as base material. Marker implantations were performed using (i) 60Ni⁺ at 180 keV to a fluence of 10¹⁶ at./cm², (ii) ¹⁹⁷Au¹⁵⁺ at 190 MeV to a fluence of 4 · 10¹³ at./cm² at 90 deg (normal to the surface) or (iii) 5 · 10¹² at./cm² at a rather shallow incident angle of 19 deg to the surface. Subsequent oxygen PIII experiments were performed at process temperatures between 450 and 600°C. Analysis of the samples was performed using secondary ion mass spectrometry in a time-of-flight setup with 15 keV ⁶⁹Ga⁺ ions for the analysis and 1 keV Cs⁺ ions for sputter profiling.

In the present experiment, amorphisation by 190 MeV Au should be completed at the higher fluence of 4 · 10¹³ at./cm², whereas a transient state with a partial amorphisation should exist at the lower fluence of 5 · 10¹² at./cm² when the literature data for 350 MeV Au is extrapolated to 190 MeV. For 180 keV Ni implantation, a total of about 3900 displacements per incident ion along the whole track, according to SRIM, translates into a value of nearly 35 dpa, which should lead again to an amorphous state in the first 100-150 nm of the NiTi bulk material. However, differences in the oxide layer growth during subsequent oxygen PIII experiments are observed (see Figs. 1&2): The growth of the oxide layer depends not only on whether the surface region is amorphous but also whether it was amorphised by electronic or nuclear energy deposition.

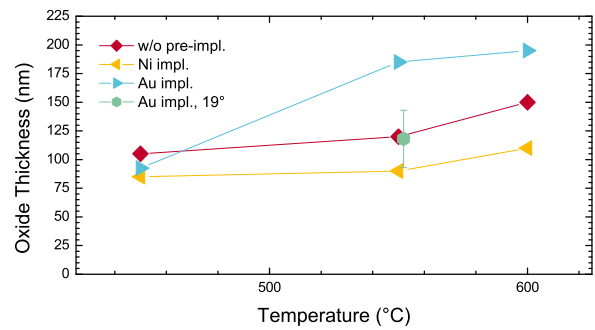


Fig. 2: Oxide thickness as a function of temperature and ion pre-implantation. Native NiTi without pre-implantation is indicated as w/o

It could be speculated whether two different amorphous states - differing in the partial radial distribution functions - are reached by Ni and Au pre-implantation into bulk material or whether Ni implantation leads only to a strongly disordered intermetallic compound and amorphisation - as the final state - occurs only for Au implantation or at even higher fluences for Ni implantation. For the second scenario, the reduction in diffusivity would be caused by the atomic disorder whereas the amorphisation leads to an enhancement as the atomic structure will be, at least, partially more open. Detailed investigations using either XANES or TEM are necessary.

References

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doi: 10.1016/j.nimb.2009.01.068

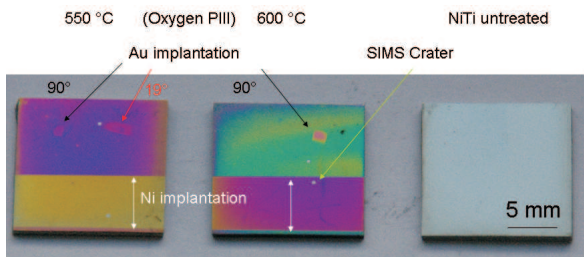


Fig. 1: Optical view-graph of samples after and before oxygen ion implantation. The lower part corresponds to the Ni implantation, the small spots to the Au implantation. SIMS craters with 300 x 300 μm² size are visible in some parts of the samples.