Institute for Ion Beam Physics and Materials Research

Forschungszentrum Rossendorf

Surface Modified NiTi for Improved Biocompatibility

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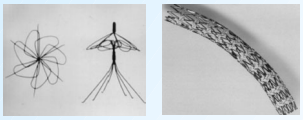
Memory Shape Material Nitinol (NiTi)

Advantages

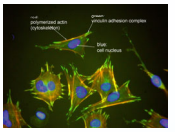
- ✓ Alloy of 50% titanium und 50% nickel with memory shape or superelastic properties
- ✓ In general excellent biocompatibility due to naturally formed TiO_2 surface proven *in vitro* and *in vivo*.
- ✓ In use in medical applications:
  - ✓ vascular stents
  - ✓ vena cava filters
  - ✓ osteosynthetic devices mainly in craniosurgery.

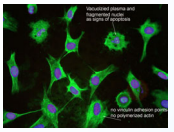


Vena cava filters (left) and coronar stents (right) of nitinol are already in clinical application

Problems

- O In some cases corrosion in vivo demonstrated
- O Cytotoxicity in case of insufficiently oxidized surface
- O Concerns because of high (50%) concentration of nickel in the alloy
  - O Allergic
  - O Toxic
  - O Carcinogenic





Rat bone marrow cells on stainless steel (left) show well polymerized actin cytoskeleton and vinculin adhesion complexes. On nitinol of one provider there is no organization of the cytoskeleton, cells undergo apoptosis.

→ A corrosion resistant NiTi surface without nickel release is demanded

- ✓ **Formation of a Ni depleted surface layer**
- ✓ **Increase of the surface layer stability**
- ✓ **A barrier creation against the Ni release from NiTi alloy**
- ✓ **No change of bulk properties**

Concept and Method

For Plasma Immersion Ion Implantation (PIII) negative high voltage pulses are applied on a conductive substrate in a physical plasma

- → Implantation of ions of the plasma into the surface (up to 50-100nm) without modification of the bulk
- → Approved for hardening of surfaces or corrosion resistance
- → Parallel to the implantation erosion of the surface by sputtering occurs

Pure nickel gets more sputtered by argon ions in PIII than pure titanium

- → Investigation, whether surface nickel depletion of nitinol by preferential sputtering is possible

Substrate: commercial polycrystalline **NiTi alloy** (**55.90 wt.% Ni** and **44.08 wt.% Ti**) produced by Memory – Metalle GmbH

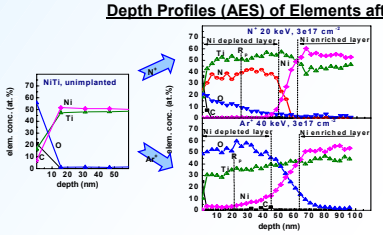
Ion Implantation:

- ➢ RF-discharge as a plasma source
- ➢ high voltage pulses: H = **400 Hz**, **τ = 5 µs**
- ➢ ion energy of **20 - 40 keV**
- ➢ ion fluences of **(3-5)x10^{17} cm^{-2}**
- ➢ temperature below **200 °C**

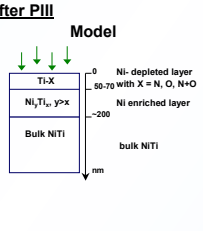
Analysis: Auger Elecron Spectroscopy (AES), Potentiodynamic corrosion measurement, Cell culture, ^{125}I fibrinogen adsorption, F1+2, SC5b-9 Elisa

Physical Properties

Depth Profiles (AES) of Elements after PIII

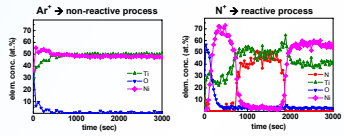


Model



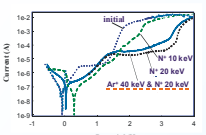
PIII of N into NiTi leads to a Ni depletion of a 50nm surface layer down to <1% Ni and formation of a Ti(O,N) layer. Below is a broad Ni enriched layer. This is not compatible with the preferential sputtering model.

Depth Profiles After High Energy Beam Line Implantation



Sub-surface ion implantation of the inert element Argon has no effect on the Ni profile (left). Sub surface implantation of N (right), which excludes sputtering leads to Ni depletion in the implanted area, flanked by Ni enriched areas. This strongly suggests a reactive/ diffusion process.

Corrosion Properties in Ringer Solution

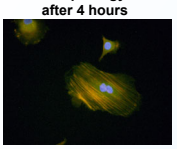


The implantation leads to an increase of the corrosion resistance: the corrosion current decreases and the corrosion potential increases.

Biological Properties

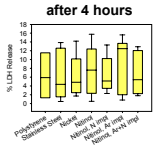
Behavior of Bone Forming Cells

Morphology after 4 hours



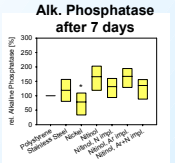
Formation of cytoskeleton and adhesion complexes, no signs of apoptosis

LDH Release after 4 hours



No obviously increased cell death or immediate toxicity

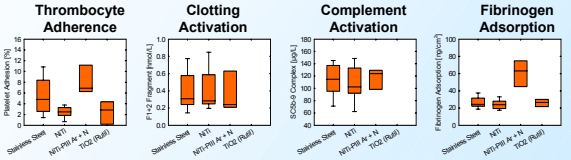
Alk. Phosphatase after 7 days



No inhibition of cell differentiation and specific activity

The nickel depleted nitinol surfaces exhibit good compatibility for bone forming cells and can be recommended for orthopedic implants.

Behavior in Contact with Blood Components



The nickel depleted nitinol surfaces showed a strongly increased adsorption of fibrinogen, what is in parallel with an increased blood platelet adherence. Clotting and complement cascade did not get activated by this surface. Application in this field so far does not seem favorable.

Summary and Conclusions

- ✓ Plasma immersion ion implantation of Ar^+ and/or N^+ ions into nitinol is a useful technique to decrease the surface Ni concentration to less than 1%.
- ✓ The Ti(O,N) surface prevents corrosion and out-diffusion of Ni ions
- ✓ The mechanism is more a reactive, diffusion mechanism than preferential sputtering
- ✓ From the current biological tests the surfaces can be suggested more for orthopedic implants than for cardiovascular implants.

Literature:

Shevchenko N., Pham M.-T., Maitz M.F. **Studies of surface modified NiTi alloy.** Applied Surf Sci (2004) (***in press***)

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