6 Summary and Outlook

6.1 Summary

The NiTi shape memory alloy is a potential candidate for biomedical application. The excellent mechanical properties make them more suitable compared to other implant materials. As a biomaterial, corrosion resistance and biocompatibility are among the important parameters. However, the presence of high concentration of Ni (50 at%) make them scrutinised for its biocompatibility (risk of Ni leaching out). It is well known that the surface stability dictates the corrosion and biocompatibility properties of NiTi. The current study was aimed to tailor the surface, in-order to enhance the biocompatibility and corrosion resistance of NiTi.

A systematic bottom up approach starting from removal of the material and oxide growth was performed to modify the surface of NiTi. A combined approach based on electrochemistry and high temperature process was utilised.

6.1.1 Electrochemical methods

Electropolishing of NiTi was realised using methanolic 3 M sulfuric acid. Electropolishing renders a flat, bright and Ti enriched surface. Electropolishing also leads to the formation of a stress free surface, which would further facilitate the homogenous growth of barrier oxides. The mechanistic behaviour of electropolishing was ascertained.

The linear polarisation studies in this solution reveals that the passivity of NiTi lies between that of Ni and Ti. Ni exhibits active-passive behaviour whereas both NiTi and Ti show passive behaviour. The electro-dissolution of NiTi in methanolic 3 M sulfuric acid solution shows an equivalent dissolution of Ni and Ti. Further experiments are certainly required for better understanding of the dissolution behaviour.

The rotating disc electrode (RDE) studies were performed to ascertain the electropolishing mechanism. The studies revealed that, the electro-dissolution is mass transport limited. The electropolishing of NiTi follows a salt film mechanism, i.e. dissolution product is the rate limiting species. The electrochemical impedance spectroscopy (EIS) confirms the formation and presence of the compact salt film during electropolishing. Surface characterisation in terms of morphology and chemistry reveals, electropolishing as a promising technique for modifying NiTi surface. The modification depth by electropolishing is in the order of nanometers.
6.1.2 High temperature methods

High temperature methods were used to achieve higher depth of modification i.e, in the order of micrometers. An approach based on selective oxidation and selective chloridation (degasing) was utilised. The concurrent oxidation (TiO$_2$) and sublimation (chloride compounds) of two elements of different affinities (NiTi) lead to the formation of Ni free thick TiO$_2$. The kinetics of the reaction varied with the temperature. At 700°C, a paralinear behaviour was ascertained. A parabolic growth of oxide and a linear mass loss due to evaporation of the chloride compounds, resulted in a paralinear behaviour. The treatment resulted in a Ni free homogenous oxide (TiO$_2$). The cross-sectional analysis showed a layered structure, with 40 µm thick TiO$_2$, followed by a diffusion zone, Ni$_3$Ti of 50 µm thickness. Such a modification enhances the biocompatibility of NiTi.

Surface modification was carried out in a reducing environment of N$_2$ and H$_2$. The resulting composition of the surface strongly depends on the temperature. At 600°C, the surface was covered with particles of titanium oxide. At 800°C, the surface turned golden yellow colour due to the formation of TiN. The segregation of Ti to the surface and inward diffusion of N$_2$ leads to the formation of TiN. Most notably, the XPS analysis revealed that the TiN layer is devoid of Ni (approximately to a depth of 100 nm). Also, TiN is well known for its biocompatibility and tribological property.

6.1.3 Passivity breakdown and cavitation erosion behaviour

To understand the repassivation behaviour under dynamic loading, a tensile rig coupled with an electrochemical cell was designed and fabricated. However, a clear picture on the behaviour could not be ascertained due to certain technical difficulties. Tribological aspect was performed using a cavitation erosion setup. The erosion resistance of NiTi was compared with Ni and Ti. NiTi shows a better erosion resistance.

6.2 Outlook

“One faces the future with one’s past.”

Electropolishing in methanolic 3 M sulfuric proves to be a promising method to obtain a stable NiTi surface. This experimental conditions can be extended to other NiTi based alloys, namely NiTiCu.

The electropolishing follows a compact salt film mechanism. During electropolishing a salt film is formed at the electrode - electrolyte interface. The chemical composition of the salt is unknown (assumed to be a compound formed by the dissolved cation and the anions in the
electrolyte). An in situ technique would help to understand the chemical composition of the salt film formed. Many researchers follow an in situ technique based on synchrotron radiation to analyse the salt film formed during the pitting [100, 101]. A similar study can be utilised to understand the salt film formed during electropolishing of NiTi.

The high temperature modification methods proves to be a promising method. The experiments in reducing atmosphere can be modified in terms of the temperature, holding time.

An effort to study the repassivation behaviour of thin oxides under tensile load can be modified in order to work with thicker oxides. Also the repassivation behaviour of the alloys can be ascertained by designing electrochemical set up in a cavitation erosion system.