Surface treatment of NiTi for medical applications

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Summary

This article gives an overview of methods applied for surface treatment of nickel–titanium shape memory alloys in medical applications. The different methods are classified into the three major groups: *removal, oxidation* and *coating.* The principle behind each group of methods is explained and the pros and cons of the different methods are discussed.

Keywords

Introduction

The near equiatomic binary alloy Nickel-Titanium (Nitinol) NiTi can reversibly change between two crystal structures. These two crystal structures are the low temperature martensitic phase, which is monoclinic and has B19 symmetry, and the high temperature austenitic phase that is cubic with B2 symmetry. The transformation between these two phases is responsible for the extraordinary mechanical properties which make the material so interesting. The reversible transformation upon loading and unloading is called pseudoelasticity. The ability to revert to an impressed high temperature shape is called shape memory effect [1].

Materials with these extraordinary properties are often referred to as smart or intelligent materials. The interest in this material for medical applications has been steadily growing during the last years. It is presently used for orthodontic arch wires [2], for coronar stents [3] and osteosynthesis clamps [4]. A lot of other applications have been proposed or are under development, which will without doubt lead to a further increase in the use of this material [5]. This work discusses the motivation and the necessity for a proper surface treatment of NiTi. It explains the

benefits resulting from a removal of material, an oxidation or the application of various kinds of coatings.

Motivation and necessity for surface treatment

Preparation of devices from NiTi is possible by casting, reforming or even sintering of powder. A large number of mechanical procedures that remove material may be applied such as sawing, cutting, spark eroding, laser cutting, milling, drilling, deburring, electrochemical machining or grinding. Reforming methods are also applied such as pressing, folding or rolling, often combined with a thermal heating to impress the intended shape. Each of these methods makes its own specific alterations to the material and in particular to the surface or surface near bulk. Despite all attempts to apply near net shape techniques, by far most of the products are still prepared in a route that includes several preparation steps.

Beside the mechanical properties of the bulk material the surface structure is of crucial importance for the applicability of the material. This general fact is particularly true for NiTi in medical applications as it prevents unintended side reactions.

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Sufficient corrosion stability is in general indispensable for a material's applicability. Titanium which is also used for medical applications such as implant material is electrochemically very base. In aqueous solutions and in contact with air it reacts rapidly and forms a dense homogeneous layer of titanium oxide that protects the metal from further environmental access. A review of the phenomenon of passivity can be found in the Encyclopedia of Electrochemistry [6]. Nickel is nobler than titanium but the alloy's behaviour is mainly determined by the titanium oxide. This is why NiTi is generally found to be sufficiently corrosion-resistant in body fluids such as blood or saliva [7]. The possibility of increasing the corrosion resistance by oxidation or coating is discussed in detail in the following chapters. Attention must be paid to incompatible combinations of materials under which the corrosion resistance can be drastically reduced. This is the case for orthodontic NiTi arch wires in contact with fluoride containing mouthwashes or toothpastes [8, 9]. They are still often recommended to patients in order to compensate difficulties in oral hygiene.

Directly linked to the above mentioned corrosion resistance is the release of nickel from NiTi alloys. Such a nickel release can cause allergic or toxic reactions. With respect to the vital importance for any medical application of NiTi special emphasis has been paid to its biocompability [10–20]. The formation of a stable barrier of titanium oxide is essential for a successful prevention of this release. This is discussed in detail in the chapter on oxidation. A recent and more sophisticated method combines a selective dissolution of nickel from the alloy with a subsequent oxidation [21].

A major limitation of the investigations carried out so far is the separate testing of chemical and mechanical material performances [22–24]. NiTi with its excellent mechanical properties is covered by a thin oxide film with a thickness of nanometer or micrometer. The elastic properties of these films are much worse compared with the bulk material. Cracks are easily formed during use, which can result in a local attack causing local corrosion.

Classification of surface treatments

It is useful to first classify the methods available for the surface treatment and discuss the principles. Figure 1 classifies available methods of surface treatment as follows:
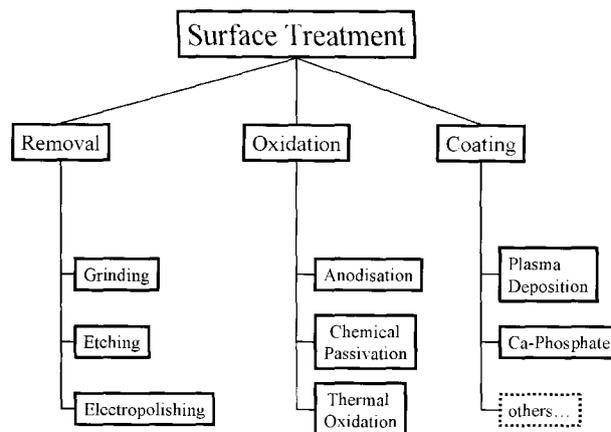
- Removal
- Oxidation and
- Coatings.

Figure 1. Classification of surface treatments applied to NiTi discussed in this article.

Removal

This first class of methods includes those which remove material. It is further subdivided into

- mechanical grinding,
- etching and
- electropolishing.

A local removal of material is necessary to achieve its final shape. Also, deburring requires a significantly higher local removal. The homogeneous ablation may also be necessary to remove material that has different mechanical properties. This is e.g. the case if the NiTi alloy was molten in a graphite crucible. As a result the carbon content is higher which leads to the formation of thermodynamically stable TiC inclusions but also changes the phase transformation temperature. Removal of an existing oxide layer is another important motivation. These oxides are usually the result of a thermal oxidation. This is e.g. the case if shaping of the wires is performed by thermal heating or by inherent electrical resistivity heating of wires in air contact.

Mechanical Grinding

The grinding of NiTi is performed as it is on other metals. All types of grinding tools such as emery paper, grinding sponges, rotating brushes, emery pastes and emery emulsions are applied. As usual mechanical grinding is performed stepwise starting from a coarse treatment with subsequent refining of the emery. The particles employed are hard materials such as aluminiumoxide (Al_2O_3), siliconcarbide (SiC), silicionoxide (SiO_2), zirconiumoxide (ZrO_2), tungstencarbide (WC), boroncarbide and diamond. The final

step of mechanical surface treatment may be mechanical polishing. There is a very common misuse of the terms grinding and polishing in the literature. Grinding with fine particles is often referred to as polishing. However, the removal of material through an abrasive process is grinding. This is true even if very fine diamond slurries with particle size of e.g. 100 nm are used. Polishing on the other hand is a mechanical process that encourages the surface mobility of material to achieve a smoothing of the surface.

The exceptional mechanical properties of NiTi, namely its phase transformation ability under mechanical stress, is responsible for the difficulties in proper surface preparation. Each single emery particle will apply a mechanical stress to the surface in a microscopic or nanoscopic dimension. Depending on the local surface topography, angle and shape of particle and the force applied, parts of the material will be removed. The shape memory alloy may undergo a reversible local phase transformation under mechanical load preventing the intended removal of the material. This behaviour is responsible for the lower efficiency of mechanical grinding on NiTi as compared with other metals. The aforementioned property is also the reason that mechanical polishing of NiTi is not the method of choice.

Mechanical grinding introduces a significant deformation to the outer layer of the SMA. As a rule of thumb the depth of influence scales with the size of the particles. The subsequent refining of the emery is sufficient to remove scars from the coarser emery but it is usually insufficient to remove the whole layer that was mechanically deformed.

Etching

An alternative to mechanical surface treatment is etching. This chemical dissolution of material has some advantages. It does not cause any mechanical stress to the material. The etching conditions can be carefully adjusted in terms of chemical aggressivity and temperature. Consequently a selective removal of oxide layers from the alloy becomes possible,

since the chemistry and hence the dissolution kinetics of oxide films is entirely different.

An etching strategy includes three aspects, shift of pH-value, oxidation and complexation. A shift of the pH-value or the use of aggressive agents increases the dissolution rate. This becomes possible in acidic or alkaline solutions. The thermodynamic stability of a material with respect to the pH-value can be taken from the Pourbaix-diagram [25]. Metal dissolution is usually encouraged in an oxidising environment since the reaction

$$Me \rightarrow Me^{n+} + n\ e^- \qquad \text{eq. 1}$$
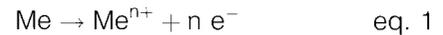
produces the metal cation which can be solvated and thus dissolve the metal. Under highly oxidising conditions, however, a kinetic hindrance the so called passivation can prevent further dissolution. This is discussed in the following chapter. Complexation of ions increases the effect of etching by lowering the efficient concentration near the surface. This results in a higher chemical gradient followed by a faster dissolution. One example of an etching solution useful for NiTi is composed of 10 ml HF, 20 ml HNO_3 and 30 ml H_2O [26]. Alkaline etching can be performed in 4 M aqueous KOH for 30 min at 120 °C or in saturated aqueous $Ca(OH)_2$ solution in an autoclave at 170 °C for 20 h. The etching rate also depends on the local properties of the alloy such as crystallographic orientation, grain structure and, in case of multi phase materials such as a partly transformed NiTi alloy, also on the crystallography itself. A very nice example is the appearance of pseudo-martensite bands in plain martensite on a partly phase transformed material shown by Pohl *et al.* [27]. An anisotropic etching behaviour produces surfaces showing a higher attack in grain boundaries and on some grains. The resulting surface often clearly displays the grain structure of the material. Different grains can have significantly different heights and roughness. Figure 2 shows a schematic of the various geometric parameters such as roughness, grains, grain boundaries and graves.
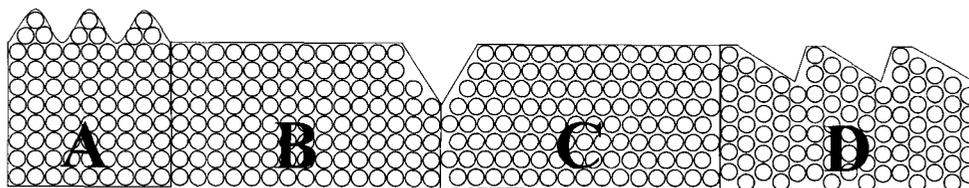

Figure 2. Schematic of the various geometric parameters such as roughness, different crystallographic orientation of grains, grain boundaries and graves.

A special case is the electroetching were the etching is supported by an electrical current which is discussed in the chapter on electropolishing.

Chemical polishing

Chemical polishing requires an aggressive solution with properties similar to that employed for etching. The difference is the higher dissolution rate to ensure saturation within the solution in the direct vicinity of the material. The concentration gradient normal to the surface under polishing conditions allows a distinction between the different surface features. As shown in Figure 2, small surface elevations extend into a region of lower concentration. Consequently the dissolution rate is higher. This finally leads to a levelling of the surface and thus to a smooth surface. The tendency of Ti to passivate itself makes it difficult to chemically achieve these polishing conditions. Electropolishing is therefore much more common.

Electropolishing

Electropolishing is based on the aforementioned principles. The main advantage is the easy control of the dissolution rate or dissolution conditions. The work piece is anodically polarised in a solution that chemically dissolves the material. Anodic polarisation drives the equilibrium in equation 1 to the right side, which means that the alloy dissolves. The dissolution rate will increase with increasing potential until a saturated layer forms in the direct vicinity of the metal. The dissolution rate is no longer controlled by the charge transfer, but diffusion-controlled. Within a thin electrolyte layer of about $10\,\mu m$ the concentration gradient drops from saturation to bulk solution concentration. An elevated part of the metal sticks into this concentration gradient and "sees" a lower concentration. As a result the dissolution rate is not diffusion-controlled and therefore higher. In this manner a levelling and thus a smoothing of the surface is finally achieved. At higher potentials side reactions such as oxygen evolution or electrolyte oxidation become more important or dominant. The simple controllability makes electropolishing so convenient. The process can be either performed potentiostatically, i.e. reaction controlled, or galvanostatically, i.e. rate controlled.

Electropolishing of NiTi is often performed in mixtures of alcohol and acids such as 33% nitric acid in methanol at $-30\,°C$ [28], 5% perchloric acid in ethanol at 38 V [26] or sulphuric acid in methanol [29]. Fushimi *et al.* performed electrochemical impedance spectroscopy to demonstrate that the electropolishing of NiTi follows the compact salt film mechanism [29].

An interesting feature can result from the phase transformation of the alloy. If the material is polished in its martensitic form the surface can display a martensitic relief after transformation [26]. This should be taken into consideration when planning a surface treatment route for NiTi devices in production or research.

Oxidation

The high oxygen affinity of titanium is responsible for the formation of oxide films on NiTi [6]. These films are effective barriers against corrosion or nickel ion release. Hence, it is of interest to thicken the oxides. On the other hand thermal oxidation is performed during thermal shape imposing of e.g. orthodontic arch wires by electrical resistivity heating. A detailed knowledge of the underlying mechanisms allow the production of tailored oxides being optimised in terms of thickness, structure, composition, nickel gradient, conductivity, permittivity, semi conducting properties, mechanical properties, adhesion and corrosion resistance. There are three ways to form oxides:

- anodisation,
- chemical passivation and
- thermal oxidation.

A schematic of oxide formation on NiTi is given in Figure 3. The figure is true to scale taking the Goldschmidt radii as basis. The alloy is covered by a thin oxide layer which is in contact with an oxygen supplying phase that can be either water or air. A chemical gradient or an electrical field drives the metal cations through the oxide towards the outer oxide interface. Oxygen anions on the other hand are driven under the same conditions inward to the metal/oxide interface. The less noble titanium has a higher chemical gradient. The driving force for the titanium is therefore higher than that of nickel. The oxide growth is coupled to the stoichiometry between cations and anions since otherwise local space charge layers are formed within the oxide. The resulting gradient is schematically visualised in Figure 3 by a decreasing share of nickel in the outer part of the oxide. Several investigations have confirmed the fact that nickel is enriched at the metal/oxide interface or at the inner part of the oxide in both cases of anodic and thermal oxidation [21, 30].

Anodisation

Oxide formation of NiTi by anodisation must be performed in an electrolyte of low aggressivity that allows the material to be passivated. This is usually an aqueous solution of a diluted mineral acid such as
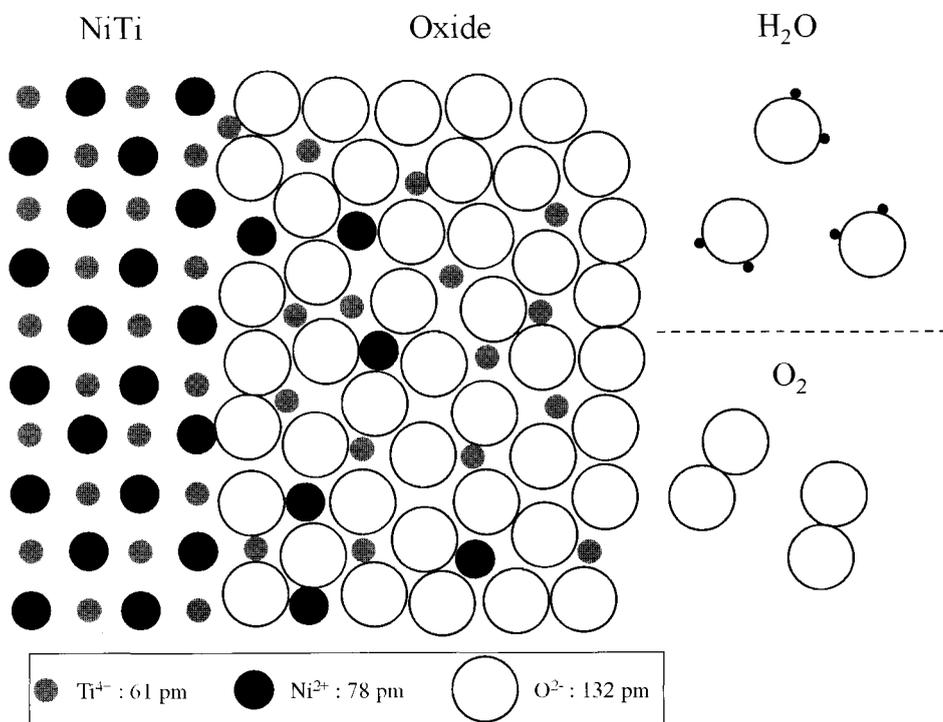
Figure 3. Schematic presentation of the oxide formation on NiTi. The figure is true to scale based on the Goldschmidt radii of the ions.

sulphuric acid or a solution of near neutral pH-value or even better, a buffered solution (acetate buffer, borate buffer). The work piece and the counter electrode are immersed into the solution and the NiTi is polarised anodically. This anodisation can be performed potentiostatically (at a constant potential), galvanostatically (supplying a constant current) or potentiodynamically (linear increase of potential with time). This anodisation is performed either in a two electrode (working electrode, counter electrode) arrangement with a power supply or in a three electrode (working electrode, counter electrode, reference electrode) arrangement and potentiostat which allows a much more precise potential and growth control.

The alloy to be anodised is always covered by a thin native oxide film resulting from the contact with air or electrolyte. This initial film thickness is usually in the range of a few monolayers with a thickness of 1–3 nm [6]. The potential applied will drop over this thin isolating (or semiconducting) oxide layer resulting in an enormous field strength of around 1 GVm^{-1}. For comparison, the ionisation field strength of dry air is around 3 MVm^{-1}. As a result metal cations are emitted from the metal/oxide interface into the oxide and oxygen anions are emitted from the electrolyte/oxide interface into the oxide. These ions are travelling via inter lattice vacancies in a field assisted thermally activated process following

the Cabrera-Mott-model. When reaching the opposite interface new oxide is formed resulting in an increase of oxide thickness. This results in a decrease of the field strength which is the driving force for the oxide formation. This so-called high-field mechanism of oxide growth is quite well understood and allows preparing tailored oxides.

Firstly the film thickness can be precisely controlled by applying a certain potential or current. Since oxide formation is a self inhibiting process, differences in oxide film thickness will be levelled. The electrostriction of the oxide layer under the high field strength on the other hand reduces the number of defects. Most precise control with the lowest concentration of defects is achieved under potentiostatic conditions. Under potentiodynamic or galvanostatic conditions the properties depend on the scan rate or current density respectively. Higher values result in higher defect concentrations. An advanced anodising procedure allows to control the gradients of nickel and titanium within the oxide. It becomes possible to form an oxide layer that consists of nickel oxide as an inner layer and of titanium oxide in contact with the environment [21].

Chemical passivation
Chemical passivation requires a strong oxidising agent. Commonly used for NiTi are solutions of nitric

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acid with concentrations of 10% [31] or 20% at 80 °C applied for 20 min [30]. Another way is boiling in perhydrol (30% H_2O_2) for e.g. 60 min. The advantage of chemical passivation is its simple application. The work piece is immersed into the passivation solution for some time, rinsed with water and is then ready for application. This method can be easily utilised for standard applications where sufficient passivation is achieved with this method.

Thermal oxidation

The formation of a thin native oxide film in air contact is strictly speaking a thermal oxidation in an atmosphere (dry or wet) of 20% oxygen 80% nitrogen at a temperature of 298 K. In fact thin native oxide films are always formed. However, the term thermal oxidation is usually only applied for processes above 200 °C. A borderline case is thermal treatment in wet air or water steam as in autoclaves used for sterilisation. The temperature is very moderate between 100 °C and 200 °C but this also leads to an increase in film thickness on an untreated sample. Even boiling in water will cause an increase of the film thickness.

Temperature, oxidation time and composition can influence thickness and composition of the scales formed during thermal oxidation. Obviously prolonged oxidation leads to thicker films. An increase in temperature accelerates the oxidation. Different oxidation behaviour is observed below and above 500 °C [32, 33]. An outer nickel rich layer is formed at temperatures of 500 °C or 600 °C [33, 31]. The medically favourable depletion of nickel in the outermost oxide layer can be further encouraged by a selective oxidation of titanium in an atmosphere with a lower oxidation potential [31]. The extensive use of this strategy results in a titanium depletion of the alloy near the metal/oxide interface. This can actually lead to the formation of a zone of Ni_3Ti phase or Ni_3Ti precipitates in NiTi [34, 33, 31]. An advanced attempt to overcome this limitation is a selective dissolution of nickel from the outermost layer of NiTi in solution followed by an oxidation which results in a NiTi alloy with an oxide of low nickel content [35, 36].

Coatings

In medical applications coatings on NiTi are usually applied to increase the material's biocompatibility. Especially for applications such as implant material an adhesion of cells should be favoured; this can be achieved by depositing calcium phosphate. Other approaches are the implantation of ions or surface

nitriding in order to increase wear and corrosion resistance. Finally an uncommon method is introduced to implement a function into the oxide.

Calcium phosphate

Calcium phosphate coatings are favourable in terms of surface treatment for NiTi as an implant material. Such a coating must have a sufficient adhesion to NiTi, being mechanically stable to withstand both the strong bending of the superelastic SMA and the shape memory transition under thermal cycling. Calcium phosphate coatings have proven to fulfil these requirements. Essential for these properties is a microcrystalline and porous structure. This can be achieved if the coating is deposited from an oversaturated solution. The oversaturation guarantees continuous nucleation and therefore leads to microcrystalline structures with a good adherence of human cells. Successful application was reported for a supersaturated calcification solution composed of 1.8 mM K^+, 3.0 mM $H_2PO_4^-$, 6.0 mM NO_3^- which yielded a 10 µm layer after 24 h immersion at 20 °C [37, 38].

Plasma coatings and implantation

Plasma is a highly reactive gas phase. At the interface to an adjacent solid phase, in this case the NiTi surface, unusual reactions take place. The plasma can be produced by electrical discharge or by microwave excitation. Highly reactive species like molecules in excited state, atoms, molecule fragments or even radicals initiate reactions resulting in good adherent and chemically stable surface layers. An alternative approach is ion implantation in which ions such as oxygen or nitrogen are accelerated in an electrical field to be implanted into the material of interest. Several of these techniques have been already applied to NiTi [39, 40]. When planning such a method special attention should be paid to select a non-line-of-sight technique which means that the coating source creates an environment that coats the whole work piece and not only the side that faces the source.

Other types of coating

Special types of coatings may become necessary now or in future for extraordinary applications. A comprehensive discussion would go beyond the scope of this article and just one example shall be given here. Radionuclides of yttrium and indium were implemented as conjugates in coatings of hyaluronan diethylenetriamine pentaacetic acid to functionalise NiTi for application in endovascular radiotherapy [40].

Conclusion and outlook

NiTi with its extraordinary mechanical properties pseudoelasticity and shape memory effect is a material that has already gained significant importance for medical applications. The surface treatment of this material was classified into three groups. Removal of the material removes the alloy and also oxides and yields smooth surfaces of defined roughness. Chemical, electrochemical or thermal oxidations produce passive films of desired thickness, structure and composition making the material corrosion-resistant even in biological environments. These oxides also act as barrier for the release of nickel ions. This is also one of the function of coatings. Improved adherence of biological cells, improved corrosion and wear resistance and implementation of specific functions are other approaches that will improve the performance of NiTi in its various applications.

The anticipated extension of application fields has already triggered novel surface treatments for NiTi. Knowledge based electropolishing for selective elemental dissolution of Ni from NiTi or smart anodisation to form pure TiO_2 are presently under investigation. Also methods for the chemical deposition of strongly protecting layers e.g. from organic solutions or from ionic liquids are presently under development.

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