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Nitinol Surfaces for Implantation

Svetlana Shabalovskaya, Gianni Rondelli, and Markus Rettenmayr

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Nitinol, a group of nearly equiatomic Ni-Ti alloys, steadily conquers new areas of application. Because of the need to keep a low profile of miniature implant devices, and considering the lack of compatibility between Nitinol superelasticity and the mechanical properties of traditional coatings, bare surfaces are of interest. In this article, an overview of our studies of bare Nitinol surfaces is presented, and the performance of coated surfaces is outlined. Together dense and porous Nitinol offer a wide array of surface topographies, suitable for attachment and migration of biological cells and tissue ingrowth. Native Nitinol surface oxides vary from amorphous to crystalline and exhibit semiconducting properties associated with better blood compatibility. Nitinol surfaces are analyzed with regard to high and lasting nickel release in vitro. Surface oxide thickness and Nitinol intermetallic particulates are discussed in relation to corrosion resistance and mechanical performance of the material.

Keywords advanced characterization, biomaterials, coatings, corrosion testing, failure analysis, intermetallics, titanium

1. Introduction

Owing to mechanical compatibility with living tissues (Ref 1), Nitinol is suitable for a diverse field of implantation from cardiovascular to orthopedics. The biocompatibility of Nitinol, however, is constantly challenged because of high content (up to ~56% by weight) of Ni, known for its toxic and allergenic effects (Ref 1). High Ni content of these alloys does not imply high Ni release in the body (Ref 2). However, the knowledge on Ni release from Nitinol evolves. Earlier studies on the alloys prepared under laboratory conditions showed a reduction of Ni release to almost undetectable levels after 10-14 days of exposure to physiological solutions. In contrast, recent results obtained for certain commercial materials used in as-received wire and sheet forms (Ref 3, 4) demonstrated that Ni release may significantly increase with time up to six months (more references in (Ref 2)). This correlates well with the complications after implantation of Nitinol ASD (Atrium Septal Defect) closure devices attributed to Ni release and sensitivity reaction (Ref 5). What are the sources of Ni release? Nitinol as an intermetallic compound is stable, and Ni is not readily soluble as in the case of Ni-rich alloys or pure Ni (Ref 1). Furthermore, due to a gain in the formation energy, Ti oxides prevail over Ni oxides on Nitinol surface providing good biocompatibility associated with their inertness. Chemically homogeneous surfaces with an optimal thickness would protect Nitinol against corrosion and Ni release. However, this is not always the case. Importantly, with the miniaturization of Nitinol devices, the role of the surface in the implant performance is increased. In this article, we overview our studies of Nitinol surfaces related to their safe biological performances. It is not our goal, however, to provide here a detailed review of the literature on this topic. Our corresponding chronological reviews focused on various Nitinol's aspects and all the references can be found elsewhere (Ref 1, 2, 6, 7).

2. Performance of Bare Nitinol Surfaces

Comparative analysis of the corrosion resistance of strained Nitinol demonstrated that bare surfaces outperformed coated ones and those modified with energy sources (Ref 7). Bare surfaces also offer low profile for the miniature devices and variable thrombogenicity (Ref 2), important for cardiovascular applications. At present, the chemistry of Nitinol surfaces can be varied in a wide range providing Ni content from zero to about 30% (Ref 1). Although in the latter case Ni is bound into an oxide, these surfaces should not be used for medical applications since they proved to be as toxic as pure Ni (Ref 1). Low Ni concentrations are easily achieved by means of simple surface treatments, such as electropolishing, chemical etching with subsequent boiling in water, anodizing, and brief heat treatments (Ref 8).

Nitinol surface topographies can also be largely modulated (Fig. 1) rendering desirable cell responses. For example, electropolishing of NiTi in different states, austenite versus martensite, results either in smooth or structured surfaces (Fig. 1a, b). Elimination of inclusions and precipitates using chemical etching results in surfaces more suitable for cell attachment and migration (Fig. 1c, d). The structured surfaces associated with the R phase (Fig. 2a), as opposed to the B19' surface martensite (Fig. 1b), may be more appropriate for certain applications. As one can see from the AFM images

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Svetlana Shabalovskaya and **Markus Rettenmayr**, Institute of Materials Science and Technology, Metallic Materials, University of Jena, Loebdergraben 32, 07743 Jena, Germany; and **Gianni Rondelli**, Institute of Energy and Interphases, Center of National Research, Milan, Italy. Contact e-mail: svetinol@yahoo.com.

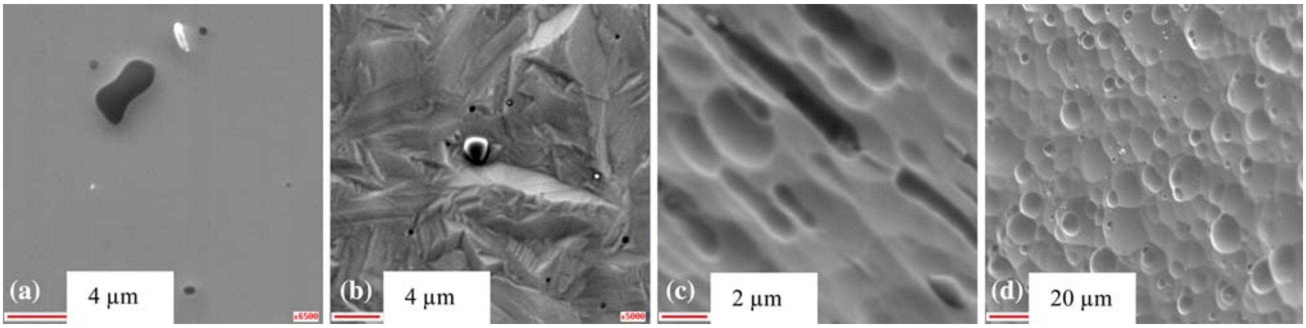

Fig. 1 SEM images of Nitinol surfaces electropolished in austenitic (a) and martensitic (b) states; wire etched in HF + HNO_3 solutions—lateral side (c) and cross section (d). Adopted and reprinted from Ref 7

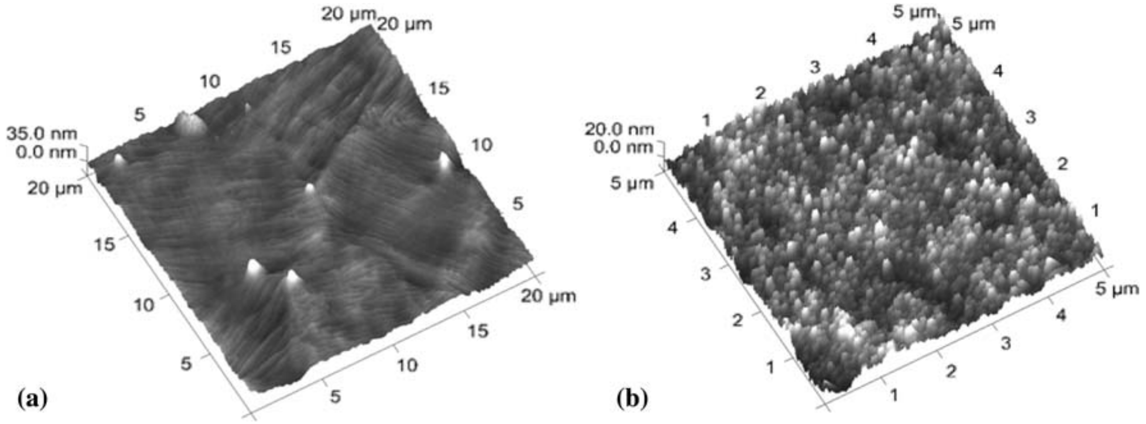

Fig. 2 AFM images of mechanically polished surface (a), and chemically etched plus heat treated in air for 20 min at 500 °C (b). Peaks observed on the image (a) correspond to the hard particulates protruding through the surface. Ti dioxide crystallites of a 20-30-nm size were formed during heat treatment (b). Adopted and reprinted from Ref 7

(Fig. 2), Nitinol surfaces differ significantly in their topography on a nano scale level. Heat treatments of the material promote growth of Ti dioxide crystals that may reach 20-30 nm in size after a brief exposure to 500 °C (Fig. 2b) (Ref 2). According to recent studies (Ref 8), chemically etched Nitinol surfaces are amorphous, and the surfaces heat treated at 500 °C are crystalline, and both are semiconductive with the band gaps of 3.4 and 3.0 eV, respectively. Electropolished surfaces are also semiconductive with a band gap of 3.4 eV (Ref 9). Anodizing of Nitinol to generate new surfaces is also being explored (Ref 8) (see other Ref in 7); the increase of polarization resistance up to 67 MΩ cm^2 can be achieved by anodizing.

Porous Nitinol with permeable structural network and desirable degree of porosity is another material suitable for bone substitute (Ref 1, 2, 6). The living tissues grow directly into the body of porous implants transforming it into a new material. It has been shown that after three months, a newly formed implant-bone composite acquires the properties superior to those of the original alloy and the bone. New bone in the porous Nitinol is detected as early as 2-3 weeks after implantation. The performance of porous Nitinol has always been found to be similar or superior to pure porous Ti or its alloys (Ref 2, 6).

3. Nickel Enrichment of Surface and Interfaces

High and lasting ion release observed sometimes in vitro is an indication of Ni accumulation in Nitinol surface. There are quite different avenues that can lead to this outcome. Thus, high temperature treatments of the material to improve its mechanical properties or to anneal lattice defects after plastic deformation are accompanied by alteration of the phase composition of the alloy. Various binary Ni_xTi_y phases as well as their oxides can be formed and, as a result, the composition of the adjacent matrix alloy is altered. This affects not only the mechanical properties of Nitinol but also the phase transformation temperatures, corrosion resistance, and Ni release. During the production of wires, Nitinol is subjected to numerous drawings with intermediate annealing at the temperatures up to 700 °C and higher. This material has a heavily oxidized lustrous surface, which is sometimes considered for medical applications. Indeed, the external surface layers may have relatively low Ni content. However, a seemingly low Ni content may not ensure an inert surface behavior. Thus in Fig. 3, the TEM images of NiTi wires with original surface are shown (Ref 10). Wire (a) had less than 1% Ni and wire (b) approx. 7% Ni on the surface. Both wires showed the increase

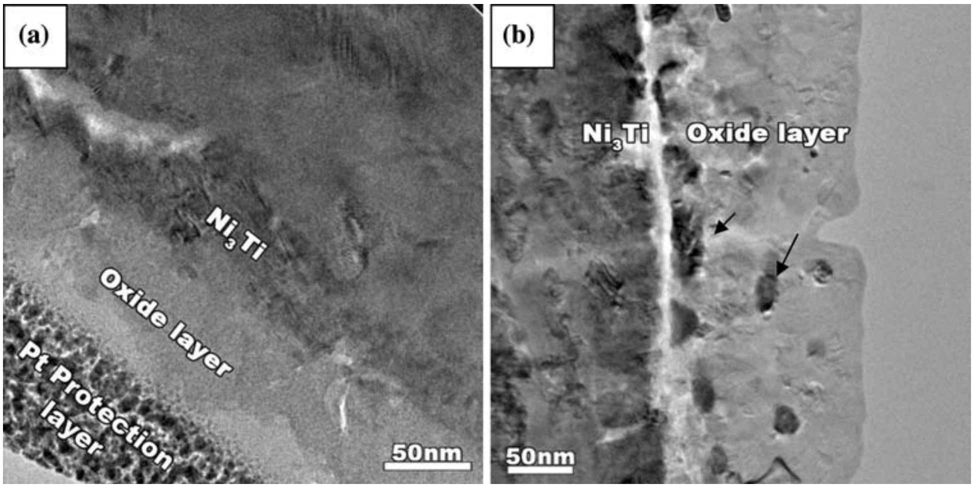

Fig. 3 TEM images of the surfaces of two Nitinol wires with original oxides. Formation of a thick Ti-based surface oxide layer resulted in the enrichment with Ni of the interface between the surface and the bulk of the alloy: Ni_3Ti layer on both images (a and b) and Ni particles marked by arrows (b). Adopted and reprinted from Ref 10

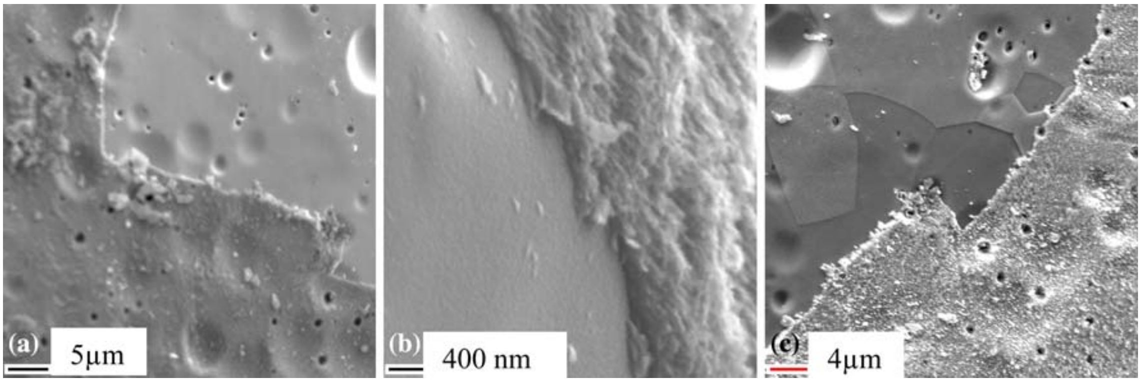

Fig. 4 SEM images of Nitinol surface pre-treated using a routine protocol developed for pure Ti for deposition of a CaP coating (boiling in 30% hydrogen peroxide with subsequent etching in 4 M KOH solution at 120 °C for 30 min). Adopted and reprinted from Ref 7

of Ni release with immersion time, but the Ni release from wire (b) increased to 1.8 mg/L after six months and exceeded that from wire (a) by as much as 100 times (Ref 10). For comparison, human blood serum contains 1-6 µg/L of Ni (Ref 2). In addition to differences in the surface topography, these wires also revealed differences in Ni chemical state and its distribution in the surface. In wire (a) there was only an intermediate Ni_3Ti phase formed between the bulk of the alloy and the Ti surface oxides. In wire (b), however, there was also segregated pure Ni in agreement with the earlier studies of Nitinol oxidation behavior (Ref 11-13). The Ni particulates of 10-100 nm diameters adjacent to the Ni_3Ti layer and located as close as 20 nm from the surface were observed. This Ni reservoir is easily activated in corrosive environments and can be a cause of associated allergenic reactions observed after Nitinol implantation (Ref 5). These surfaces showed low breakdown potentials (200 mV) (Ref 10) implying the need for their optimization before implantation.

Surprisingly, another avenue, which may lead to Ni accumulation in the surface, is associated with the low temperature protocols developed for pure Ti, aiming at the formation of thick dioxide layers. Soaking or boiling of Nitinol in hydrogen peroxide with a subsequent long exposure to alkaline KOH or $Ca(OH)_2$ solutions at temperatures from 60 to 160 °C is employed as a pre-treatment for CaP deposition. The resulting Nitinol surfaces induced Ni release (up to 9 mg/L) of as much as a few thousands times higher than that observed with bare surfaces (Ref 7, 14). The Auger study (Ref 7) revealed two layers formed during this pre-treatment (Fig. 4): an external flake-like layer less than 1 µm thick ($C_{35}Ti_{20}Ni_{12}O_{33}$) and a smooth internal layer with high Ni content ($C_8Ti_{11}Ni_{58}O_{22}$). A precise TiO_2 stoichiometry of this buried sub-layer ($Ti_{11}O_{22}$) indicates that the goal of the pre-treatment has been in fact achieved, but this also implies that the detected Ni (~58 at.%) is in elemental state and can be readily released.

The temperatures mentioned above are not high, and one does not expect a significant atomic diffusion. The situation with the atomic diffusion in surface oxides is not trivial, however. The Ti oxide layers are forming spontaneously even at room temperature, and Ni atoms are liberated from the Ni-Ti atomic bonds. These Ni atoms are defects in the Ti oxide layer. Due to the smaller size of the Ni atoms compared to Ti and oxygen atoms, Ni can easily diffuse through an interstitial path. On the other hand, because of oxygen shortage, the Ti surface oxides are commonly non-stoichiometric. The sites of missing oxygen atoms present atomic vacancies, which can also be used by Ni to

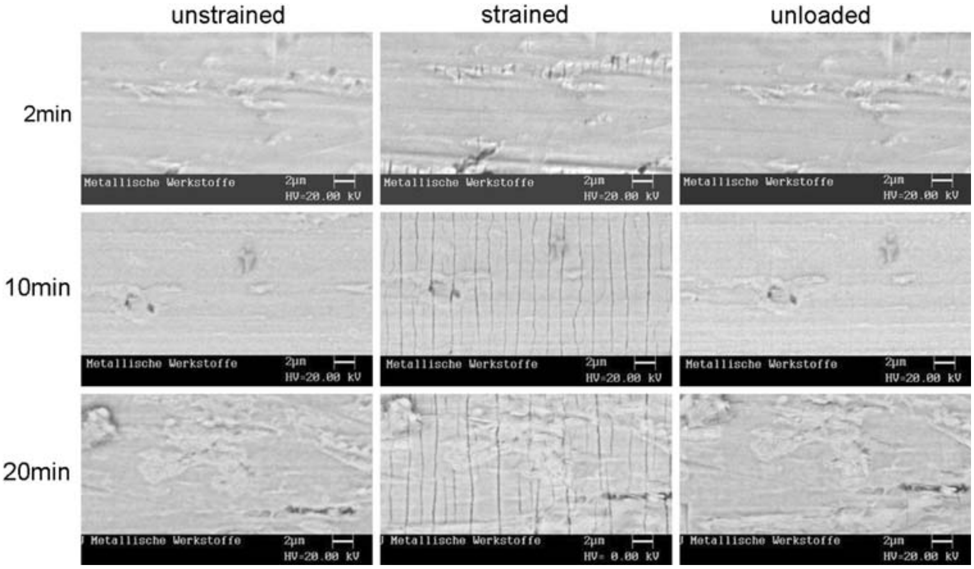

Fig. 5 SEM images of the surfaces of heat-treated, as-received Nitinol wire in strain-free, strained to 8%, and unloaded states. Adopted and reprinted from Ref 17

migrate through Ti oxides. Thus, in the presence of ready-to-use lattice vacancies, the diffusion of Ni atoms within Ti oxides may occur effectively already at low temperatures, and Ni-rich surface sublayers can be generated during long exposures.

4. The Effect of Surface Oxide Thickness

Heat treatments of Nitinol are continuously explored for Nitinol surface oxidation. There is a belief that "the ceramic-like nature of Ti dioxide must resist cracking in the pulsative oscillation" (Ref 15). Unfortunately, the ceramic nature of TiO_2 acts against both Nitinol superelasticity and cyclic pulsation regime. Ceramic materials are held together by ionic and covalent bonds, which tend to fracture before any plastic deformation occurs; superelastic deformation experienced by Nitinol is in plastic limits for TiO_2.

Being strained, thick surface oxides, which were formed during prolonged heat treatments crack (Ref 8, 10, 16, 17). There should be an optimal oxide thickness that would retain surface integrity despite its ceramic-like nature under strain and provide a barrier for Ni release. Figure 5 indicates that the surface of Nitinol wires heated for 2 min at 540 °C (30-nm oxide thickness determined using Rutherford spectroscopy) cracks at 8% strain, but only at surface inhomogeneity locations; after a 10-min heat treatment (80 nm), the whole surface is uniformly cracked in both perpendicular and longitudinal directions; further increase in oxide thickness to 100 nm results in surface flaking (Ref 17). According to the studies of the effects of heat treatments on Nitinol breakdown potentials (Ref 13, 16), this oxide thickness is on the border between high and very low breakdown potentials.

5. Surface Particulates

Nitinol is a heterogeneous material, which acquires inclusions (Ti-based oxides and carbides) during melting, and Ti_xNi_y precipitate particles through the solid state reactions during annealing. The latter phases are easily oxidized into $Ti_xNi_yO_z$. All these particulates are hard and brittle and can vary in size substantially (Ref 18, 19). While inclusions are distributed quite uniformly in Nitinol, the precipitate particles can form clusters or chains of 50-300-μm length. The type of the particle distribution in the material is essential for its mechanical strength. Because the stent wall thickness is being reduced to 30-50 μm to obtain better biocompatibility and the diameters of wires employed are around 100 μm, and because, in two-thirds of stent graft failures, were metal fractures involved (Ref 20), a special attention should be given to material optimization, which, in turn, will improve Nitinol surface.

The areas adjacent to the intermetallic particles are more vulnerable to localized corrosion because of altered chemical composition. The localized corrosion around particles was observed at potentials about 1 V (Ref 19). These potentials are much higher of those expected in the body (≤500 mV (Ref 6)). However, our analysis (Ref 2) of the images of the failed stents with very thick surface oxides 0.2-1 μm (Ref 15) revealed that localized corrosion occurs along the chains of the particulates. Although "the next-generation Nitinol stents were improved and only minimal evidences of corrosion reported, the mechanical instability is still a problem" (Ref 20), which may also be related to the surface. The analysis of elute from the grafts recovered a granular material of 0.5-2.5 μm identified as 'nickel-free titanium oxide' (Ref 20). The accumulation of intermetallic particles of the size comparable to the cell's size (~2 μm) due to corrosion in the areas adjacent to the implants is a possibility that needs to be considered. Fortunately, the thickness of the fibrous membranes formed around Nitinol by the eighth week of implantation were only 21 versus 24 μm for stainless steel and 425 μm pure Ni (Ref 21). This implies low Nitinol toxicity involved.

6. Surface Coatings and Modifications

Coatings and modifications of native Nitinol surfaces aimed at the design of a barrier for Ni release in the human body have been widely explored (Ref 7). The situation with the Nitinol implant devices, which are expected to perform in the superelastic regime, is not trivial. It was observed in situ that electropolished NiTi surface withstood 8% of tension without cracking, but coated or ion-implanted surfaces lost their integrity at lower strains (Ref 22). Surface cracking was observed at 1% strain for the nitrogen implanted and at 3% for DLC coated and Ti-sputtered surfaces. The coated or modified NiTi surfaces already in a strain-free state might not have passivity, and their corrosion resistance deteriorated under strain. Alteration of the surface topography and the heterogeneous distribution of local strains, both associated with the nature of the martensitic transformation in Nitinol, and the presence of particulates undermine coating adhesion and cohesion. Certain polymer coatings could be better choices as far as the mechanical compatibility is concerned. However, damaged polymer does not repassivate and causes crevice resulting in enhanced material corrosion. The corrosion rates for polymer coated Nitinol of the order of 13 μm/year reported in Ref 23 are significantly higher than those known for bare surfaces (0.1-2.26 μm/year) (Ref 7). In addition, in strained states, the coatings may not be effective against Ni release (Ref 7, 24). Considering the specifics of Nitinol, we believe that native surfaces appropriately passivated with optimized oxide thickness are a better choice for implantation.

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