NITINOL – A NEW MATERIAL FOR BIOMEDICAL APPLICATIONS

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Abstract: The present work surveys some of the more recent studies preformed on the chemical and physical properties of NiTi alloys (Nitinol), aiming at its use as a biomaterial. On this basis, the shape memory effect is examined, as well as the corrosion resistance of the alloy when in contact with the human fluids, both under static and dynamic conditions. It is concluded that, in spite of the enhanced mechanical behaviour, which makes the material suitable for a wide range of medical applications, the results on the corrosion resistance and biocompatibility of the alloy are still not conclusive. Therefore, more information should be collected on the corrosion behaviour of the material, giving special attention to Nitinol used under stress, after deformation and under loading/unloading conditions, to avoid the lack of predictability on the corrosion behaviour of this alloy under dynamic conditions.

Keywords: **Biomaterials, Nitinol, Corrosion Resistance, Memory Shape Effect**

1. INTRODUCTION

A wide range of metals and their alloys, polymers, ceramics and composites can be used as biomaterials in order to repair or replace living tissues or organs.

Major classes of metals used with this propose include stainless steels (316L), cobalt-chromium alloys and titanium or its alloys (Ti-6Al-4V). In order for these materials to perform successfully, they must have physical properties that allow them to achieve the function for which they were implanted [1]. Moreover, the material should present a high corrosion resistance as well as biocompatibility, i.e. the environment should not have detrimental affects on the material and the material must not adversely affect the physiological environment.

In the last decade, nearly equiatomic NiTi alloys (Nitinol) have attracted considerable interest for biomedical applications, due to the combination of mechanical properties (shape memory and superelasticity) and physical-chemical properties (biocompatibility). In addition, this alloy presents an elastic modulus which is closer to that of the bone, compared with other metal implant materials (Figure 1). A similarity in the deformation behaviour between Nitinol and the bone can also be observed in this figure, which contributes to the biomechanical compatibility of this alloy. In fact the absence of recoverable strain of stainless steel may be one of the major reasons for the fracture of orthopaedic implants in the body. Therefore, Nitinol may be used with great advantage in orthodontics, in treatment of bone fracture and in bone suture anchors for attaching soft tissues.

The shape memory effect is a consequence of a solid state phase transformation, known as martensitic transformation, that occurs with no diffusional atomic flow down a concentration gradient according to Fick`s law. Because of their nature, martensitic transformations are frequently referred to as diffusionless, displacive or shear-like. The driving forces for the martensitic phase transformation can be chemical or mechanical. Thus, martensitic transformation describes the formation of martensite from austenite (parent phase) during cooling or during loading with an external stress. If deformed and then unstressed in the low temperature martensitic condition, a shape memory alloy, will regain its original shape after heated to cause the reverse martensite to parent transformation. Strains imposed to martensite on the order of 6-8% are completely recovered. The ability to regaining the original shape is associated with the reverse transformation of the deformed martensitic (Figure 2). Other interesting mechanical behaviour of these alloys is the pseudoelastic effect, known as superelasticity, associated with the formation of a reversible stress-induced martensite. After releasing the stress, the alloy recovers the initial shape, at constant temperature (Figure 3).

The shape memory effect, or shape recover from a predeformed piece after heating, has been successfully achieved in orthopaedic practice [2,3], by using appropriate alloys where the phase transformation occurs at approximately 30°C. As an example, to fix a fracture Nitinol is cooled, stretched and wrapped around the broken bone. As it warms to body temperature the wire "remembers" its original length and tightens around the bone, beginning to compress the fracture to a greater extent than could be achieved by simply tightening the wire. In maxillofacial surgery, that often involves reshaping of the mandible and other cranial bones, shape memory bone fasteners are proving to be superior to the usual screwed metal plates. Besides the treatment of bone fractures, this alloy has been

approved for many clinical applications, including orthopaedic bone anchors, orthodontics archwires, dental implants, scoliosis correction, vena cava filters and cardiovascular endoprostheses.

The wide spectrum of application in implantology imposes special requirements, namely on the biocompatibility of Nitinol. As the Nitinol has a high nickel percent and because Ni is capable of eliciting toxic and allergenic responses, much concern exists over both these issues in the case of NiTi alloy. Release of nickel ions is the greatest problem that can be faced after Nitinol implantation.

The Nitinol resistance against corrosion, that is responsible for Ni release, ranges from excellent to poor in the body [4,5]. A recent report on the failures of 33 corroded stent/grafts retrieved after 5 to 43 months use in patients [5] calls for attention to the problem of Nitinol surface stability. Also, in studies of the *in vivo* use of orthodontic devices, several cases of severe inflammatory reactions, resulting in contact dermatitis and oral lesions, have been reported.

The corrosion resistance properties of NiTi alloys, likewise other non-noble metal implants [6], rely on the presence of a passive oxide film on the surface, which inhibits the development of uniform corrosion. However, it should be remembered that some ion release also takes place at the passive state and that breakdown of the passive film can occur both during surgery and in service life.

The *in vitro* results of corrosion studies of Nitinol are also controversial, ranging from unpredictable or poor to excellent and comparable to that of pure titanium. A great body of research on corrosion resistance of NiTi alloys has been performed by Rondelli [7-10]. Using potentiodynamic and potentiostatic techniques the corrosion resistance of Nitinol was evaluated in various media simulating body fluids and compared to that of stainless steel, Co-Cr alloys and titanium. The general conclusion is that in potentiodynamic tests, when breakdown of passive film is caused by a slowly increasing potential, Nitinol is characterized by low anodic current and no significant corrosion attack occurs above that potential. On the other hand, in potentiostatic tests, mechanically polished Nitinol reveals a localized corrosion potential inferior to that of other metal implants [10]. Moreover, these authors found out that the nickel ions release was three times higher for NiTi than for 316L stainless steel when evaluated in physiological simulating fluids, as it would be expected due to the much higher nickel content in Nitinol.

Another study, from Villermaux [11], points to the lack of reproducibility in the pitting potential values of mechanically polished NiTi samples that range from 240mV to 1000 mV. Vandenkerckhove [12], who conducted potentiodynamic tests combined with impedance spectroscopy, pointed out that Nitinol is readily passivated even in deaerated solutions, forming surface oxide layers with semiconducting nature, similar to what happens with other implantable materials, such as titanium or stainless steel [13]

Besides the lack of reproducibility found in the literature on the corrosion testing results, both in vivo and in vitro, there are other parameters that should also be evaluated. In fact, surface roughness, complex geometry, stresses and large deformations are factors that should be analyzed independently in studying the corrosion behaviour of implants [14]. Furthermore, implants in the body are working under loading/unloading conditions, being deformed in the plastic regime [15,16], but corrosion studies are mostly performed on unprocessed materials in static conditions. Stress normally aggravates ion release, resulting in a degradation of both the body environment and the implant. There are few known efforts to evaluate the corrosion behaviour of Nitinol after various deformations [17-19] and under load [8], though these studies could simulate the actual conditions of a dynamic implant working in the body under stress, sometimes being deformed beyond the elastic limit.

Studies of the effect of applied stress on the corrosion parameters of stainless steel, Co-Cr-Mo, and Ti-Al-V show that loading, even within the elastic limits, results in enhanced metal ion release [15,16,20]. When the applied stresses are higher than the yield strength, leading to plastic deformation, a decrease in the breakdown potentials and an increase in the corrosion current, with disruption of the passive surface film, occur. Bondy et al [15] attributed this observation to the fact that stressed implants have more fragile passive layers, which are more vulnerable to disruption by mechanical means than similar surfaces without stress. However, corresponding systematic studies on Nitinol are still missing.

Another important aspect related to the performance of an implant is the effect of localized wear-corrosion conditions, which causes naturally passive alloys to degrade at a rate exceeding that from wear alone. This occurs because of the succession of erosive removal of the protective surface film, followed by dissolution and by film reformation. Minimization of this process is critical to extend prosthetic device lifetime.

In order to allow for an extensive use of Nitinol, both in dynamic and in static conditions, several treatments may be envisaged, ranging from conventional coatings to more sophisticated surface modification techniques. All these treatments have in common the need of maintaining the bulk properties of Nitinol while changing its surface in a way that it becomes compatible for the use in physiological media.

On this basis, several surface treatments have been proposed in the literature in order to enhance the corrosion resistance of the material allowing, at the same time, for minimum nickel content in the oxide film. In fact, varying parameters such as oxidation media, temperature or anodising potential, it is possible to obtain Ti-based surfaces, with TiO_2 as the main oxide, or Ni-based surfaces covered with nickel oxi-hydroxides. Also more advanced surface modifications, such as oxygen plasma immersion ion implantation, have been studied [21], leading to the formation of an inner Ni-diffusion barrier that allows for the presence of a titanium oxide film at the surface.

The validation of a surface treatment should then be based on the production of a surface presenting enhanced corrosion resistance and biocompatibility, while taking into account any possible effect on the singular characteristics of the shape memory effect of the base material.
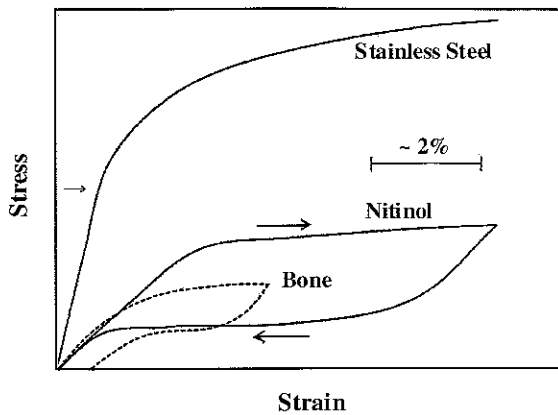
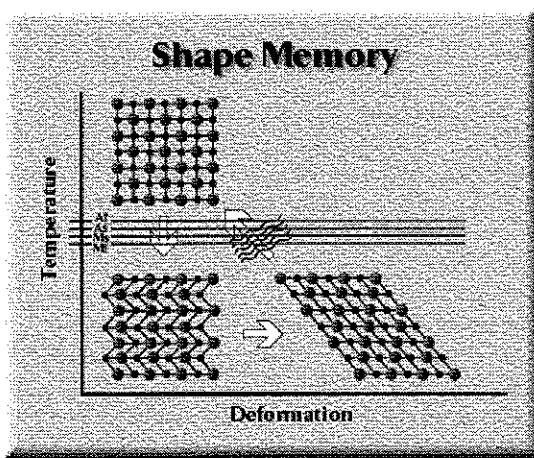**Fig.1** Schematic stress-strain diagram for bone, Nitinol and stainless steel.

Fig.2 Schematic atomic mechanism of the shape memory effect in Nitinol

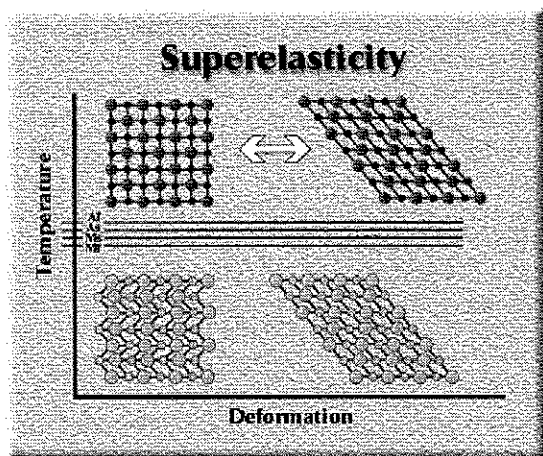**Fig.3** Schematic atomic mechanism of superelasticity in Nitinol

2. OUTLOOK AND CONCLUSIONS

Considering the physical and chemical properties mentioned above, it is possible to conclude that NiTi alloys may be

used as a new biomaterial, presenting superior biomechanical functionality. However, the use of this material in medical applications requires consolidation of scientific results, namely in what concerns its behaviour when in contact with human fluids. In fact, failure of Nitinol devices *in vivo* and the inconsistent *in vitro* corrosion performance of this alloy indicate the lack of understanding of the chemistry of native Nitinol surfaces and the absence of a standard surface treatment that could ensure stable corrosion behaviour. A comprehensive analysis of Nitinol surface and corrosion performance that are in charge of its biological response and the eventual fate of Nitinol implants are, therefore, in great demand.

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