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Relevant aspects in the clinical applications of NiTi shape memory alloys

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NiTi shape memory alloys showing pseudoelastic behaviour have great potential in dental and orthopaedic applications where constant correcting loads may be required. In most of the clinical applications the device may have been heat treated and during its life in service it will be cyclically deformed. It is therefore important to investigate the effect of cyclic straining and heat treatments upon the transformation stresses and temperatures of the material. The aim of this work is to study the thermal and mechanical ageing of a pseudoelastic NiTi shape memory alloy, as well as the environmental *in vitro* degradation of the alloy due to the effect of artificial saliva.

1. Introduction

NiTi alloy combines the characteristics of shape memory effect and pseudoelasticity with excellent corrosion resistance, wear characteristics, mechanical properties and good biocompatibility. These properties make it an ideal biological engineering material, especially in orthopaedic surgery and orthodontics [1].

The shape memory effect and the pseudoelasticity are related to a thermoelastic martensitic transformation (austenite → martensite) which can be produced by cooling or may be stress induced.

Martensite formation can be initiated by cooling the material below M_s, defined as the temperature at which the martensitic transformation begins. M_f is the temperature at which martensitic transformation finishes. The transformation is reversible, A_s being the temperature at which the reverse austenitic transformation (martensite → austenite) begins upon heating, and A_f the temperature at the end of the reverse austenitic transformation.

When a stress is applied to the parent phase material above its A_f temperature, a mechanically elastic martensite is stress-induced in alloys which exhibit thermoelastic behaviour. That is, the deformed material reverts to its original shape when the stress is released. This effect is called the pseudoelasticity effect or superelasticity [1–3].

The stress necessary to induce the formation of stress-induced martensite (SIM) is a linear function of temperature. The critical stress $\sigma^{\mathrm{SIM} \rightarrow \mathrm{AUS}}$ increases with increasing temperature while the yield stress of the parent phase decreases with increasing temperature. Hence, above a certain temperature plastic deformation of the austenite occurs before stress-induced martensite can be formed [4].

The size of the hysteresis (i.e. the difference between $\sigma^{\mathrm{AUS} \rightarrow \mathrm{SIM}}$ and $\sigma^{\mathrm{SIM} \rightarrow \mathrm{AUS}}$) reflects the amount of irreversible process taking place during the formation of stress-induced martensite [5–6].

When the applied stress is released below the A_s, the shape change produced remains since reverse rearrangements of twins and martensite variants has not ocurred. However, upon heating through the A_s to A_f temperature range the material regains its original shape by a reverse transformation from martensite to austenite. Thus, the original shape of the parent phase is obtained and the "deformation" of the martensitic phase recovered, this is known as the shape memory effect.

It should be noticed that if we subject the alloy to excessive deformation, the martensite is plastically deformed by slip processes and that plastic deformation is, of course, not recoverable on subsequent heating.

Some possible applications of shape memory alloys are connectors, temperature control devices, orthodontic dental archwires, intracranial aneurism clips, a *vena cava* filter, contractile artificial muscles for an artificial heart, orthopaedic implants, and other medical devices [5, 7, 8].

In most clinical applications the device may have been heat treated, and during its life in service it will be cyclically deformed. It is therefore important to investigate the effect of cyclic straining and heat treatments upon transformation stresses and material temperatures. On the other hand, as the device is designed to work in physiological conditions, nickel and titanium

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release when placed in an artificial saliva medium at 37 °C is an important parameter to study.

2. Experimental methods

The chemical composition of the NiTi alloy studied was 48% Ti and 52% Ni in atomic percentage. The transformation temperatures were determined 24 h after this heat treatment. The flow calorimeter used here measures differential signals (ΔT) by means of thermobatteries. Temperature was measured by means of standard Pt-100 probe. All signals were digitized through a multichannel recorder linked to a microcomputer.

2.1 Effect of load cycling

Fatigue tests were carried out on an electromechanical Universal testing machine working at a crossbar speed of 10 mm/min. The specimens tested were cylinders of 2.5 mm in diameter and 150 mm height. The guage length of the specimens were applied up to a 3% of maximum strain.

The stress–strain curves were recorded for each cycle with an adequate software. These curves were used to obtain the residual deformation values, as a function of the number of cycles and the variation with the number of cycles of the critical stress to induce the martensite transformation. The transformation temperatures were measured after a different number of cycles using a calorimeter [9, 10].

2.2. Effect of thermal ageing

Samples of 3 mm in diameter and 6 mm in height were heat treated at different temperatures (150, 500 and 600 °C) during different times (0.5, 1, 2, 4 and 6 h). The hardness values and transformation temperatures were determined after the heat treatments [11].

2.3. Environmental *in vitro* degradation of NiTi

Three nickel-titanium archwires for orthodontics with the same chemical composition were placed in separate bottles containing 500 ml of artificial saliva.

The simulated saliva medium consisted of 0.4 g NaCl, 1.21 g KCl, 0.78 g $NaH_2PO_4.2H_2O$, 0.005 g $Na_2S.9H_2O$, 1 g urea $[CO(NH_2)_2]$ and 1000 ml distilled and deionized water. This artificial saliva formula was used by Barret *et al.* [12]. The pH of the artificial saliva was adjusted to 6.75 with 10 N sodium hyrdroxide. The pH value coincides with that reported for human saliva [13, 14]. The samples were placed at 37 °C for 1, 4, 24 and 48 weeks.

Nickel and titanium analyses were performed with an inductively coupled plasma-mass spectometry (ICP-MS).

3. Results and discussion

3.1. Effect of load cycling

The stress–strain curves at different numbers of cycles were used to obtain the variation of critical stress, necessary to produce the superelastic effect and to determine the optimum working stress for the alloy. Fig. 1 shows the difference between the critical stress for the first cycle and the critical stress for a cycle N, as a function of the number of cycles. Fig. 2 shows the evolution of the permanent deformation values against the number of cycles.

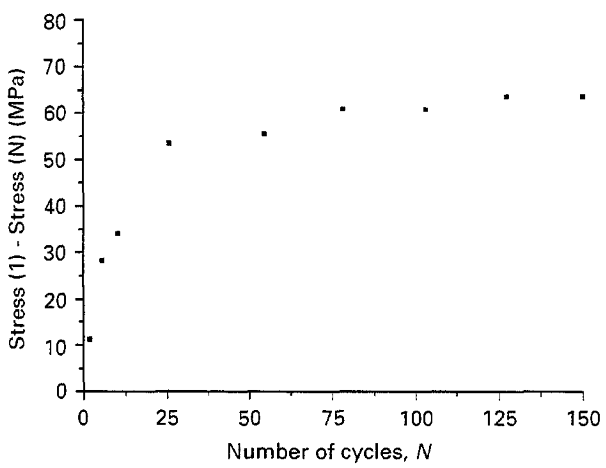

Figure 1 Difference between the critical stress (austenite → SIM) for the first cycle and the critical stress for a cycle N, as a function of the number of cycles.

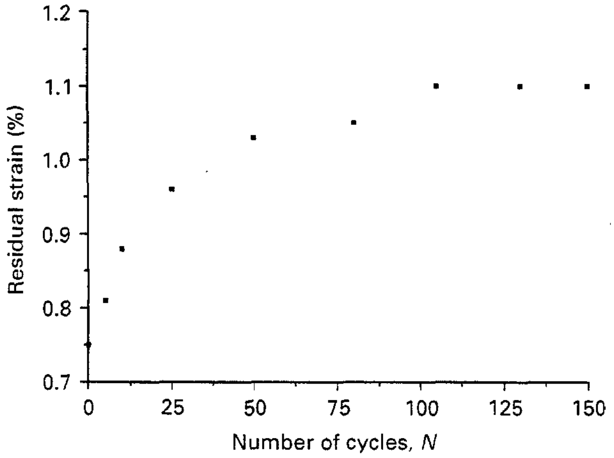

Figure 2 Residual strain evolution with the number of cycles.

As can be seen from Fig. 1, the critical stress required to induce the martensitic transformation decreases with the number of cycles and from Fig. 2 it is clear that the residual deformation increases with the number of cycles up to saturation. The reason for the residual deformation is probably the dislocation glide which obstructs the retransformation of the martensitic phase to austenite. The internal stresses created by dislocation slip may favour the formation of stress-induced martensite (SIM) [15, 16]. For this reason the critical stresses required to induce the superelastic effect (or in other words, to start the transformation from austenite to martensite), become smaller and smaller.

Figs. 1 and 2 reveal that both the critical stress required to induce transformation and the residual deformation become constant after a certain number of cycles. This can be explained by the effect of training

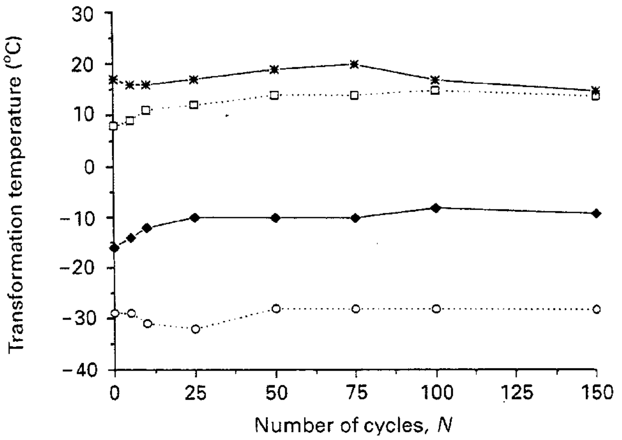

Figure 3 Transformation temperatures at different numbers of cycles □M_s; ○M_f; ◆A_s; ↽A_f.

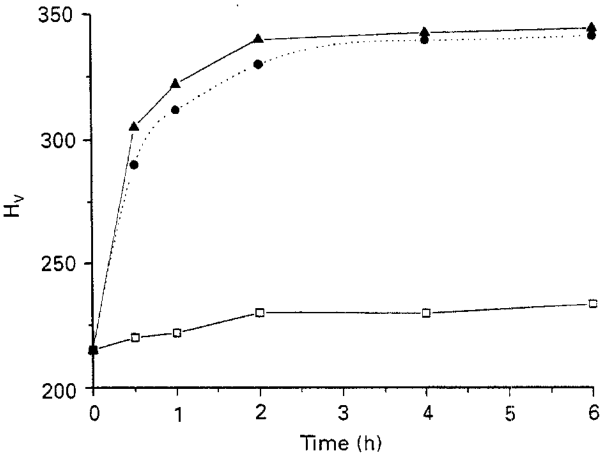

Figure 5 Evolution of Vickers hardness in relation to heat treatment temperatures and times □150 °C; ●500 °C; ▲600 °C.

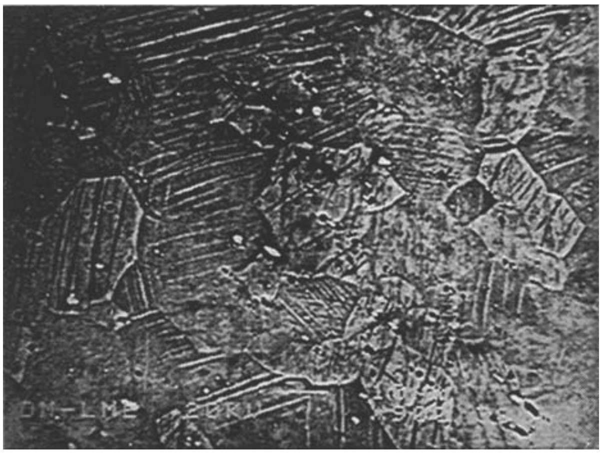

Figure 4 SEM micrograph of stabilized martensitic plates inside of austenitic grains $N = 150$ cycles.

or the two-way shape memory effect due to the introduction of oriented dislocations, mainly during the cycling processes [17-19].

The transformation temperatures in relation to the load cycles are shown in Fig. 3. As can be seen, M_s temperature increases while the transformation stress decreases with the number of cycles. This can be explained by the arrestment of martensite plates by dislocations, inducing the nucleation of new plates at M_s and producing an increase in the transformation temperature.

In Fig. 4 the stabilized martensitic plates are shown for a sample tested at $N = 150$ cycles. The number of stabilized martensitic plates increases when the load cycles increase, producing therefore a rise in the A_s temperature.

The saturation transformation stress and saturation residual strain should be known and taken into account when using a shape memory alloy with pseudoelastic behaviour in applications where the device has to endure cyclic strains. After a certain number of cycles, the device could be working pseudoelastically at a stress level much lower than that for which it was initially designed.

3.2. Effect of thermal ageing.

Direct quenching in water from 950 °C resulted in a fully austenitic structure with a Vickers hardness of 215 H_V. The austenite can be transformed during heat treatment by precipitation of $Ti_{11}Ni_{14}$ [18, 19].

The heat treatment of these austenitic specimens produced different degrees of precipitation depending on temperature and heating time. Hardness evolution with annealing is shown in Fig. 5. At each temperature the curve of hardness versus heating time has a sigmoidal shape, indicating that precipitation of $Ti_{11}Ni_{14}$ from austenite occurs by nucleation and growth processes controlled by atom diffusion [18, 20].

At low annealing temperatures (150 °C) precipitation starts after long heat treatment times. At 4 h, precipitation starts but is incomplete, as is shown by the low value of hardness. At high temperatures (500 and 600 °C) the decomposition of the austenitic phase reaches completion. This fact is reflected in the high saturation value shown by the hardness, 340 H_V. This precipitation causes an important variation in chemical composition and consequently on temperatures and stresses of transformation. After 6 h heat treatment at 500 °C and 600 °C, the samples lost the shape memory and pseudoelastic effects. The specimens that contained precipitates did not show calorimetic signals for the phase transition (austenite → martensite) when cooling the samples above M_s temperature.

The shape memory effect and pseudoelasticity can be recovered with heat treatment at 900 °C for 30 min because the precipitates are dissolved.

3.3. Environmental *in vitro* degradation of NiTi

The results of nickel and titanium release in the simulated saliva medium are shown in Fig. 6. From these results, it can be seen that the rate of nickel released is higher than that of titanium.

Comparison of nickel release from the appliances with stainless steel archwires to those with nickel–titanium archwires revealed no significant differences in the nickel levels at all time periods [12].

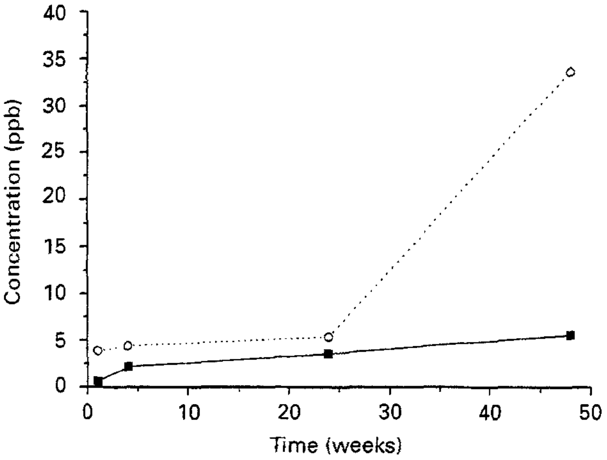

Figure 6 Ni and Ti release for a NiTi archwire after different periods of time: ■Ti; ○Ni.

The total release of nickel over the 48-week period of this study was 33.8 μg/l. This release rate is moderate because the reported average daily dietary intake ranges between 200 and 300 μg/day. Nickel concentrations in drinking water are generally below 20 μg/l [21–23]. The total release of titanium over 48 weeks was 5.65 μg/l. The average dietary intake of titanium has been estimated to be 300 to 2000 μg/day and average titanium levels in drinking water have been reported to range from 0.5 to 15 μg/l [24].

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