On the properties of two binary NiTi shape memory alloys. Effects of surface finish on the corrosion behaviour and in vitro biocompatibility

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Abstract

The present paper compares the transformation behaviour and mechanical properties of two orthodontic wires of close chemical compositions. The effects of surface topography and surface finish residues on the potentiodynamic corrosion behaviour and biocompatibility are also reported. The cytotoxicity tests were performed on both alloys in fibroblast cell cultures from human gingiva using the MTT test. It is shown that the surface finish and the amounts of surface finish residues affect dramatically the corrosion resistance. Bad surface finish results in lower corrosion resistance. The in vitro biocompatibility, though not affected to the extent of corrosion resistance, is also reduced as the surface roughness and the amounts of residues increase. This is thought to be due to surface effects on corrosion and metallic ions release.

1. Introduction

NiTi-based shape memory alloys constitute an interesting group of smart alloys which enjoy an ever increasing market share as biomaterials. They are most widely used as orthodontic arch wires, stents, etc. The mechanisms of the shape memory effect are based on the thermoelastic martensitic transformation which lead, in these alloys, to highly reversible strains either under the effects of stress (superelasticity through stress-induced martensite formation) or temperature (thermal shape memory effect). Details about the mechanisms of the shape memory effect and the potential applications of NiTi alloys may be found in numerous review articles, e.g. [1–3]. The NiTi shape memory alloys usually consist of binary alloys, with Ni and Ti concentrations near the equiatomic composition. Their microstructures are generally processed using complex thermomechanical treatments in order to obtain suitable properties, e.g. thermal shape memory, superelasticity, all-round memory effect, etc. Contrary to a general view, these properties are usually not obtained via changes in the Ni to Ti ratio but more easily, starting from a common ingot composition, through the selection of appropriate thermomechanical treatment sequences which can be better controlled than the chemical composition. The transformation and superelastic hysteresis properties as well as the long-term stability are generally positively influenced by the addition of suitable amounts of the alloying elements Cu and Fe in the range from 5 to 10 wt% and from 1% to 2%, respectively [1].

The (thermo)mechanical properties of NiTi-base alloys certainly constitute the outstanding and most perceptible attribute for their use. However, in biomedical applications involving contact with live tissues, biocompatibility issues may prove as crucial (if not more) as mechanical behaviour. In a recent work [4–5], the in vitro biocompatibility of a binary NiTi and a ternary NiTiCu alloys has been investigated using epithelial [4] and fibroblast [5] cell cultures. It has been shown that biocompatibility is negatively influenced by the presence of Cu which has been explained in terms of Cu ions release. Usually the biocompatibility of NiTi alloys has been inferred from their high corrosion resistance [6–10]. The corrosion resistance may, however, depend on factors such as surface finish quality, the amount of residues and the degree of homogeneity of microstructures. All these factors are known to affect...
the corrosion resistance of metals via establishing corrosion elements which may then lead to higher metal ions release and consequently to higher cytotoxicity. Due to the complex thermomechanical processes the NiTi alloys have to undergo and to the compelling cost reduction, it is thought that the surface finish and microstructure may not always be of good quality. In fact, in a broad survey of 25 commercial arch wires from different suppliers, bad surface finish has been found in the majority of them, with deep grooves, surface finish residues like silicon and aluminium oxides, wear residue from drawing dies, etc. [11]. This gave the impetus for this investigation which compares the properties, including corrosion behaviour and biocompatibility, of two NiTi arch wires of close chemical compositions but different surface finish.

2. Materials and methods

The alloys studied are “Neosentalloy F 80” (GAC), hereafter designated Neosent, and SE NiTi (G&H), hereafter designated SeNiTi. The samples were in the form of arch wires with rectangular sections of 0.57 × 0.42 mm². For the different investigations, the straight ends of the wires were used in the as-received states. The chemical compositions of the alloys were determined in an analytical scanning electron microscope (SEM) (Philips XL 30, EDAX SUTW Spahire detector) using energy-dispersive spectroscopy (EDS) analysis. The following compositions (in wt%), which have been determined with an accuracy of ±0.1% using a standard NiTi alloy of known composition, were found: Ni57.6Ti42.4 for Neosent, and Ni57.8Ti42.2 for SeNiTi. Metallographic investigations were conducted on electrolytically polished (Lectropol-5, Streuers) specimens in a solution of 5% HClO₄ in ethanol under 38 V and 1.1 A. To reveal microstructure, the specimens were etched in a solution of 10 ml HF, 20 ml HNO₃ and 30 ml H₂O.

The transformation behaviour was investigated using differential scanning calorimetry (DSC, Perkin Elmer Pyris I) in the temperature range from −80°C to +80°C at a rate of 10 K/min. The samples weighing approximately 10 mg were gently cut and ultrasonically cleaned in acetone before testing. A base line was recorded before each test run. Three batches were tested for each alloy with, however, reproducible results in the range of accuracy of the system (±1 K).

The mechanical properties were investigated in 3-point bending tests (Synergie, MTS, 10 N load cell) using a beam length of 12 mm. The load vs. deflection curves were recorded at 37°C. Heating of the specimens was conducted in an oil bath of constant viscosity in the range of the temperature investigated. The temperature was controlled to ±0.5°C using a closed-circuit cooler/heater (hetofrig, Heto). In order to show the effects of loading and unloading cycles on the mechanical properties, 5 cycles were generally performed.

The corrosion properties were investigated using potentiodynamic testing in a Ringer solution (Merck, pH 7) at 22°C and 37°C, and a voltage scan rate of 10 mV/s. A saturated calomel electrode was used as a reference. The solution was changed for every test run. For each alloy, 3 specimens were tested to verify the reproducibility of the results.

The biocompatibility of the chosen alloys was characterized by means of the in vitro MTT cytotoxicity test on cultured fibroblast cells from explants of human gingiva. Healthy gingival tissue explants from 5 subjects (not treated for orthodontic failures) aged between 33 and 59 years, have been used for this purpose. Right after excision, the explants were cut into cubes of about 1 mm³, and cultured in z-MEM (supplemented with 10% FCS, 2.5 μg/ml amphotericin B, 100 U/ml penicillin and 100 μg/ml streptomycin, BIOCHROM) in sterilized non-treated culture dishes (FALCON), at 37°C, and 5% CO₂. The medium was changed every 72 h beginning with the fifth day after seeding. Approximately 11 days after seeding, the fibroblasts were subcultured. The cell monolayers were removed by treatment with 1.5 ml Trypsin/EDTA (0.05/0.02%, BIOCHROM) per dish. Subsequently, the suspension was centrifuged for 7 min at 120 g. The supernatant was carefully aspirated and the cells resuspended in fresh RPMI 1640 (Gibco BRL) (supplemented with 10% FCS, 2.5 μg/ml amphotericin B, 100 U/ml penicillin and 100 μg/ml streptomycin, BIOCHROM).

Used in the MTT test, 10⁴ cells were seeded per microwell.

When used in the MTT test, the tested alloys were cut into pieces of 5 mm length, 0.42 mm thickness and 0.57 mm height, cleaned ultrasonically in absolute alcohol and then heat sterilized at 120°C for 20 min.

For the cytotoxicity determination of the tested alloys, the method of Tada et al. [12] was applied. The test was performed in sterile 96-microtiter plates (COSTAR) at 37°C and 5% CO₂ equipped with 2 pieces (10.38 mm³ active surface) of the tested alloys. The filtered MTT solution (100 μl/well, 5 mg/ml) was added to the cell cultures (i) 24 h after seeding, (ii) 48 h after seeding and (iii) 72 h after seeding. Four hours after the MTT addition, cell lysis and formazan solubilization were started by adding 100 μl of the lysing buffer (10% SDS in 0.01 N HCl pH 3.5) and incubating the plates for 20 h at 37°C and 5% CO₂. Wells containing cells but no alloys were used for negative controls (NCs). The positive controls (PCs) consisted of cells containing wells, where the addition of the MTT solution and lysing buffer were inverted. For each alloy
blanks containing the metal, but no cells, were prepared. All experiments were carried out in triplicate. Prior to the determination of the formazan formation by absorption measurements at 550 nm in a microplate reader (DYNATECH, MR5000), 175 μl supernatant of each well were transferred into a new plate. The incoherent background was determined by absorption measurements at 630 nm. Background, due to the absorption of the medium and MTT was corrected by subtracting each blank from the corresponding sample.

3. Results

3.1. Transformation behaviour

Fig. 1 illustrates the DSC curves of the alloys investigated, and Table 1 shows the transformation temperatures. The Neosent is characterized by the R-phase transformation on cooling with the typical low hysteresis temperature taking into account the peak to peak temperatures of the austenite and the R-phase peaks. The martensitic transformation is shifted towards lower temperatures. The endothermic peak denotes the austenitic transformation with an austenite finish temperature of 33°C. The transformation behaviour of SeNiTi offers a more complex picture. Two well-separated endothermic peaks are observed, which suggests that the specific thermomechanical treatments used for this arch wire might have resulted in heterogeneous microstructures with different transformation behaviours. Similar results have been reported by Ohakata and Tamura [13] who show that heat treatments below 753 K subsequent to cold working lead to a double endothermic peak in the DSC curve. Unfortunately, no attempt was made to explain these results in their work.

Table 1
Transition temperatures determined from the DSC curves

<table>
<thead>
<tr>
<th>Wire</th>
<th>$M_T$ (°C)</th>
<th>$M_F$ (°C)</th>
<th>$R_T$ (°C)</th>
<th>$R_F$ (°C)</th>
<th>$A_s$ (°C)</th>
<th>$A_f$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neosent</td>
<td>−59</td>
<td>−23</td>
<td>15</td>
<td>21</td>
<td>22</td>
<td>33</td>
</tr>
<tr>
<td>SeNiTi</td>
<td>&lt;−80</td>
<td>±72</td>
<td>−1</td>
<td>15</td>
<td>8</td>
<td>18.5°</td>
</tr>
</tbody>
</table>

*Only the high temperature endothermic peak is considered. $A$: austenite, $R$: R-phase, $M$: martensite. Start: s, finish: f.

On cooling, only the R-phase transformation is observed in the temperature range investigated, and the martensitic transformation is shifted towards temperatures below −80°C (although the beginning of the martensitic transformation may be seen in the DSC curve with an $M_s$ temperature of approximately −72°C).

3.2. Mechanical properties

The stress–strain curves determined from 3-point bending tests at 37°C are illustrated in Fig. 2. Both alloys show the superelastic hysteresis characteristic for the austenitic microstructure. A peak stress, which denotes the beginning of the stress-induced martensite transformation, can be seen in both curves. The appearance of this peak stress on loading and unloading at temperatures above $A_s$ suggests that for both alloys a critical stress has to be overcome before the austenite → martensite transformations take place, and is in many aspects similar to the Lüders deformation [14,15]. The flexure modulus is practically the same for both alloys, the strength properties are, however, very different. Comparing the loading and unloading plateau stresses given by $\sigma_{10}$ offset stresses, higher values are obtained for SeNiTi because of the thermal stabilization of the austenite phase. It can also be seen that repeated loading and unloading cycles result in a gradual softening of SeNiTi in contrast to Neosent, where practically no strength loss occurs.

![Graphs showing DSC curves and mechanical properties](image-url)
3.3. Surface topography and microstructures

Figs. 3a and b show back-scattered electron (BSE) micrographs of the surface morphology of the alloys investigated. Neosent shows a quite smooth surface with a two-phase microstructure consisting of feathery, martensitic, and blocky, austenitic areas. Homogeneously distributed second-phase particles (dark dots in Fig. 3b) which have been proven via EDS analysis to be Ti-carbides and nitrides can also be seen. In contrast, the surface topography of SeNiTi exhibits longitudinal grooves over the whole length of the wire. The dark contrast of these grooves suggests that they may be oxidized areas. Fig. 4 which illustrates elemental EDS mappings of SeNiTi reveals in fact that the surface is badly oxidized (see the oxygen elemental mapping) in the grooves and contains many surface finish residues such as silicon oxide.

Metallographic investigations of electrolytically polished and etched specimens reveal a duplex microstructure of recrystallized (smooth) and non-recrystallized (feathery), elongated grains, see Fig. 5. The general
aspect of the microstructure suggests that the feathery appearance might be due to heavy deformation with a high density of glide lines and deformation substructures (the feathery appearance is not due to martensite nor due to the \( R \)-phase because the alloy has an \( A_f \) temperature of 18.5°C). Furthermore, the presence of numerous elongated second-phase particles can be seen. All these particles show tails denoting stress accumulation and void formation at the matrix–particle interface during deformation. As for Neosent, EDS analysis of the particles shows that they consist of titanium carbide and titanium nitride.

3.4. Potentiodynamic corrosion properties

The potentiodynamic corrosion properties are shown in Fig. 6 which reveals unambiguously a higher corrosion resistance of Neosent at both temperatures. While the pitting corrosion potentials of Neosent are approximately 1.4 V at 22°C and 1.2 V at 37°C, they reach 0.5 and 0.43 V in the case of SeNiTi.

Since the alloys investigated have almost the same composition, the different corrosion behaviour results obviously from the difference in surface finish. SEM micrographs of the corrosion tested samples reveal for SeNiTi a severe corrosion attack with large pits which predominantly follow the patterns of the above-mentioned surface grooves and surface finish residues, see Fig. 7.

In contrast, the Neosent alloy surface shows only isolated areas with moderate corrosion attack and small pits which seem to be preferentially located along the rolling direction. The second-phase particles constitute also the loci of small pits, see Fig. 8.

The difference in corrosion behaviour observed is not surprising since it is well known that the quality of surface finish and the density of embedded surface finish residues (grinding and blistering particles) determine the resistance of a material of a given composition against corrosion [16].

3.5. Cytotoxicity tests

Fig. 9 illustrates the difference in the biocompatibility of the tested samples. Statistical evaluation of the results using the one-way Anova test yields a significant difference between both populations with \( p = 0.0255 \) at a significance level of 0.05. As can be seen, Neosent seems to be better tolerated than SeNiTi. The survival rate of the cells cultured in the presence of Neosent amounts to approximately 90 ± 5% for each incubation period, whereas cell cultures in the presence of SeNiTi exhibit an apparently time-dependent biocompatibility. In the latter case, a survival rate of about 77 ± 3% is observed for a first incubation period of 24 h, which raises to 81 ± 3% after 48 h and finally reaches 85 ± 3%.

Since the chemical composition is the same, the net difference in the biocompatibility is thought to arise from the difference in the corrosion behaviour of the alloys investigated.

4. Discussion

The alloys investigated in this work, although characterized by very close chemical compositions, show completely different transformation behaviour and
microstructures. This result clearly shows that the microstructure and the phase transformation temperatures of shape memory NiTi alloys can be well controlled by suitable thermomechanical treatments. The complex processing steps which introduce dislocation substructures in the material may often result in a complex transformation behaviour with the appearance of the trigonal $R$-phase and the shift of the monoclinic $B19^\prime$ martensite transformation to lower temperatures. Both alloys investigated show this behaviour. For SeNiTi, the presence of an additional endothermic peak complicates this figure still more. A plausible explanation of the presence of this peak requires a closer insight into the processing steps of the SeNiTi wire which is unfortunately not possible. Nevertheless, the presence of regions of different dislocation densities (e.g. Fig. 5) which might have resulted from low annealing temperatures, heterogeneous grain microstructures and/or non-optimized cold drawing conditions may lead to the splitting of the endothermic peak where the lower temperature peak would correspond to the regions of higher dislocation densities (the austenite phase is stabilized by work hardening). The transformation behaviour and the ability to control it is of prime interest for the practical use of NiTi alloys. Depending on the thermomechanical processing, it is possible to control the austenite finish temperature, $A_f$, in a wide range and consequently the mechanical properties. Martensitic wires, e.g. Neosentalloy, have an $A_f$ of approximately 35–37°C, and can be easily deformed at room temperature, thus allowing a comfortable handling. They develop the thermal shape memory effect at body temperature and exert a gentle load on the teeth which prevents undesirable pains for the patient, and make them the wires of choice for levelling treatments (first orthodontic treatment stages). The austenitic wires are characterized by a higher strength (compare Figs. 2a and b) and cannot be deformed permanently without destroying the superelastic effect based on the stress-induced martensite transformation. These wires develop higher loads on the teeth, and are used in later treatment stages.

The surface finish is expected to strongly influence the functionality of the wire and its lifetime. Rough surfaces may develop non-permissible friction forces between wire and bracket leading to limited development of the shape memory effect and load transmission. Furthermore, as clearly shown in the present study, the
corrosion resistance properties are badly affected by poor surface finish. The surface imperfections and impurities as they are present on SeNiTi are thought to negatively affect the properties of the passive layer thus leading to high local corrosion rates in these areas as they are evidenced by Fig. 7. These results are well in agreement with previous results reviewed by Ryhänen [17]. Trepianer et al. [18] report on the effects of surface treatment on the corrosion properties of NiTi stents and show that electropolished surfaces are characterized by a higher corrosion resistance in Hank’s solution at 37°C. Similar results have been also reported by Oshida et al. [19]. However, a direct comparison of the pitting potentials obtained in the present work with those of the references above is not possible because of different alloy compositions and testing conditions.

The in vitro biocompatibility of NiTi alloys has been also reviewed by Ryhänen [17]. It seems that depending on the test conditions, contradictory results have been reported. The general trend is, however, in favour of a high biocompatibility of NiTi alloys. In particular, Rose et al. [20] investigated the effects of NiTi on fibroblast cell cultures using the MTT test and concluded that NiTi had no effects on cell proliferation. The results reported in the present work show that mitochondrial activity is influenced by the corrosion properties. Although the alloys investigated have the same composition, the higher corrosion rate associated with the bad surface finish of SeNiTi leads to diminished in vitro biocompatibility probably due to the release of metallic ions. Gil and Planell [6] and Gil et al. [7] report on the ion release of NiTi arch wires in artificial saliva and show that the release of Ni and Ti follow a parabolic law, and lead at the end to concentrations below the daily take-up. Unfortunately, no indications were given as to the surface topography and chemistry of their wires. Wever et al. [8] also show a parabolic law for Ni ions release with an initial release rate of \(1.45 \times 10^{-7} \text{mg/cm}^2\) which then decreases rapidly due to the build-up of a TiO\(_2\) passive layer. For their investigations, they used a stoichiometric NiTi binary alloy with a well-polished surface. Based on these studies, it is thought that Ni ions release may be higher for SeNiTi compared with Neosent, particularly in the initial stages which then would lead to the observed lower biocompatibility, and the results of Fig. 9 which show a lower dehydrogenase activity for the first 24 h incubation time points to the validity of this assumption. However, more studies are needed, particularly using atomic adsorption spectroscopy, in order to correlate the corrosion behaviour with an eventual enrichment of the nutritive medium with such ions. We may conclude from the present study that more attention should be devoted to the surface finish quality of the NiTi orthodontic products and that stringent specifications, as they already exist for metallic implant materials [21], should also be worked out for these products.

5. Conclusions

The present work reports a comparative study of the properties, including corrosion and biocompatibility, of two binary NiTi42 shape memory alloys of almost the same composition. The following conclusions may be inferred:

- The alloys show different transformation behaviour and mechanical properties due to their different thermomechanical treatments.
- The alloys are characterized by a different surface finish. SeNiTi shows numerous longitudinal grooves partly oxidized, while Neosent exhibits a smooth and homogenous martensitic/austenitic surface structure which leads finally to a better corrosion resistance.
- This study shows also a significant difference in the in-vitro biocompatibility. The presence of the rougher and oxidized surface of SeNiTi and its lower corrosion resistance are thought to induce a net reduction of the dehydrogenase activity of the fibroblast cell culture.

References


