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Nickel ion release from orthodontic NiTi wires under simulation of realistic *in-situ* conditions

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The increasing use of nickel containing devices in orthodontics and the growing prevalence of nickel allergy in the population significantly increases the interest in biocompatibility studies of these devices. The decisive factor determining the biocompatibility of orthodontic wires is their corrosion behaviour. Therefore seven nickel titanium levelling arches, one titanium molybdenum, a cobalt chromium and three stainless steel wires were analysed with respect to their corrosion behaviour under realistic conditions. Potentiostatic tests to determine rupture potentials in artificial saliva and static immersion tests in artificial saliva (AS) or lactic acid (LA), as well as immersion tests with mechanical, thermal and combined mechanical and thermal stresses were performed. Subsequently, the surfaces of the wires were investigated employing scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) and the nickel release into the corrosion media of the specimens was measured with inductively coupled plasma mass spectrometry (ICP-MS). The results yield information not only about the relative corrosion tendency of the wires under *in vitro* conditions but also give a quantitative estimation about the nickel ion release of the orthodontic wires during *in vivo* treatment. Generally, the maximum release of nickel ions was two orders of magnitude below the daily dietary intake level. Mechanical and thermal loading increases nickel release in the immersion tests by a factor of 10 to 30. Two NiTi wires (Dentaurum Tensic, Forestadent Titanol Low Force) examined showed lower rupture potentials and a higher tendency towards corrosion in the immersion tests than the others due to their surface composition. However these differences are levelled off by long-term mechanical and thermal loading.

1. Introduction

With the introduction of nickel titanium (NiTi) wires into clinical practice a significant advance in orthodontic materials was achieved in 1971 [1]. In a near equi-atomic composition NiTi alloys reveal exceptional mechanical characteristics, especially superelasticity based on a phase transformation from martensite to austenite and vice versa under cyclic mechanical or thermal load [2]. Thus it is possible to design orthodontic devices with lighter and almost constant forces and with a greater working range as conventional stainless steel devices.

On the other hand aspects of biocompatibility must be considered. In the special case of an alloy, the alloy itself and all of its components have to be examined under allergic, toxic and carcinogenic aspects as the loss of each component is possible by corrosion processes and abrasion. Titanium is classified as being highly biocompatible, nickel as being uncompatible and toxic. Nickel is a very potent allergen and causes hypersensitivity reactions to a greater extent than any other metal or alloy [3]. Nickel metal, nickel sulfide, nickel oxide and nickel carbonate are definitely human carcinogenic [4]. Several papers [5–16] report that oral intake of nickel leads to recurrence and/or aggravation of nickel induced contact dermatitis. However, the effect seems to be linked to the supplied nickel dose. Contact dermatitis only arises in those cases where the nickel intake exceeds the daily dietary intake by far, which is given to be 300 to 500 μg per day. The observation that nickel-poor diet seems to cause an improvement of existing chronic contact eczemas confirms these assumptions [17, 18].

Therefore it was the aim of this study to determine the nickel ion release of NiTi wires simulating the intraoral environment in a nearly realistic manner and compare the results with reference wires made of stainless steel, cobalt chromium and titanium molybdenum. The results should be helpful for the further development of orthodontic devices under the aspects of biocompatibility.

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TABLE I Orthodontic wires used in this study (chemical composition given in atomic-%, as given by the manufacturers [4])

Manufacturer	Product	Alloy	Chemical Composition
Forestadent Pforzheim, Germany	Titanol Low Force	A_f circa 30°	Ni 51, Ti 49
Dentaurum Ispringen, Germany	Tensic	A_f circa 30°	Ni 51, Ti 49
Ormco Glendora, CA USA	Copper Ni-Ti	A_f circa 30°	Ni 45, Ti 49, Cu 6
ODS Kisdorf, Germany	Euro Arch	A_f circa 30°	Ni 53, Ti 47
GAC Bohemia, NY USA	Neo Sentalloy	A_f circa 30°	Ni 53, Ti 47
Unitek Monrovia, CA USA	Nitinol Classic	Martensite, work hardened	Ni 52, Ti 45, Co 3
Unitek Monrovia, CA USA	Nitinol Superelastic	A_f circa 20°	Ni 51, Ti 49
Dentaurum Ispringen, Germany	Remaloy	Cobalt-chromium	Co 40, Cr 20, Fe 16, Ni 15
Dentaurum Ispringen, Germany	Noninium	Nickel-free steel	Fe 72, Cr 18, C 8
Dentaurum Ispringen, Germany	Rematitan Special	TMA	Ti 78, Mo 11, Zr 6, Sn 4
Dentaurum Ispringen, Germany	Remanium	Stainless steel	Fe 72, Cr 18, Ni 8
Unitek Monrovia, CA USA	Stainless Steel	Stainless steel	Fe 72, Cr 18, Ni 8

2. Materials and methods

2.1. Materials

The wires used in this study can be split up into two groups. The first consists of seven NiTi wires, where six could be classified as being superelastic (Tensic, Titanol Low Force, Neo Sentalloy, EuroArch, Copper Ni-Ti and Nitinol Superelastic) and one was of the highly elastic type (Nitinol Classic). In the second group there are five orthodontic reference wires, a titanium molybdenum, a cobalt chromium and three stainless steel wires. Thereby a comparison of NiTi wires with orthodontic wires made of standard materials is possible. The chemical composition and the manufacturers of all investigated wires are listed in Table I. To establish standard test conditions the arch wires were tested in the dimension 0.40 × 0.56 mm^2 (0.016″ × 0.022″) exclusively. The selected wires are representative of the current market.

The wires were used as-received without any further pretreatment. A modified artificial Fusayama saliva [19] was used as corrosion medium, the composition of which is listed in Table II. Additionally, to be able to compare the results with ISO 10271, a mixture of 10 g 90% lactic acid and 5.85 g sodium chloride per liter water was also used in the static immersion test. The pH values were about 5.0 for the artificial saliva and 2.3 for the lactic acid mixture.

TABLE II Composition of the artificial Fusayama saliva used in this study

Components	(mg/l)
Sodium chloride	400
Potassium chloride	400
Calcium chloride-dihydrate	795
Sodium hydrogen phosphate-1-hydrate	690
Potassium rhodanide	300
Sodium sulfide	5
Urea	1000

2.2. Experimental setups

The measurement setup for combined loading was constructed to simulate the intraoral situation of orthodondic wires. A photograph of the complete set-up is shown in Fig. 1. The inner part of the set-up consists of two triangular bars made of macor (Macor, Corning Incorporated, NY, USA) at a distance of 10 mm.

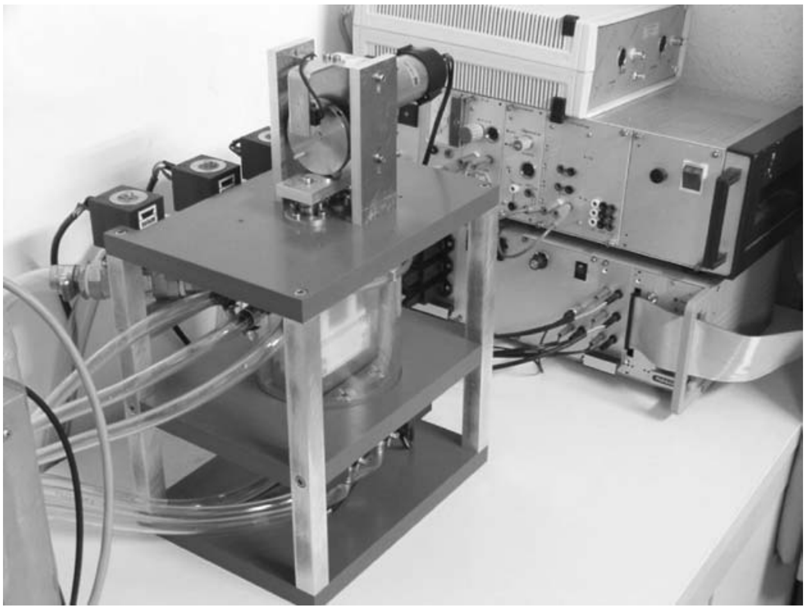

Figure 1 Experimental setup for combined mechanical and thermal loads.

Ten equal wires, each with a length of 25 mm, can be placed parallel on them. A macor stamp, displaced by an electro motor driven cam, can load the wires mechanically. A fork light barrier on the cam delivers information about how many times the stamp was driven. The mechanical set-up is surrounded by a Duran glass container (Duran, Schott AG, Mainz, Germany) filled with 0.2 l of the corrosion medium. The interior of the glass has to be inert, especially no nickel ions should be released. Therefore, no metallic parts were used, but Macor, acrylic glass and nylon screws. An acrylic glass cylinder surrounds the Duran glass container and is connected to three thermostats with a constant water temperature of 10°, 37° and 50°C, respectively. A DasyLab computer program (DasyLab, measX GmbH & Co. KG, Mönchengladbach, Germany), especially developed to control the whole set-up, regulates the water exchange of the acrylic glass cylinder through 3 pumps and 6 valves and initiates mechanical loading of the wires.

For electrochemical testing, an electrochemical cell was used with an Ag/AgCl reference electrode (Type B 2820, Schott), a platinum counter electrode, a Haber-Luggin capillary (salt bridge), a gas inlet/outlet for N2 rinsing and a temperature controlling system. The electrochemical cell was driven by a potentiostate (M Lab SCI, Bank Elektronic—Intelligent Controls GmbH, Clausthal-Zellerfeld, Germany). The setup was constructed according to ISO 10271 with two exceptions. The cell had a temperature of 37°C to simulate body temperature and modified Fusayama saliva was used as electrolyte to simulate the corrosion conditions in the oral cavity [20]. All measured potentials were converted to saturated calomel electrode (SCE) values to be compatible. A defined length of 5 cm of each of the specimens was exposed to the artificial saliva as a working electrode. Thus total wire surface exposed to the electrolyte was 1 cm^2, so the current equals the current density.

Surface and elemental analysis was performed using three further measuring instruments. An inductively coupled plasma quadrupole mass spectrometer (ICP-MS, ELAN 5000, Perkin Elmer, Wellesley, MA, USA) was used to measure the nickel ion concentration in the corrosion media after immersion tests. The detection limit of the ICP mass spectrometer is given by the manufacturer to be below 1 μg/l. Consequently the wires in the tests were arranged such that a sufficient surface of the wires was exposed to the corrosion media to expect a corresponding ion density. The structure of the surface of the immersed wires was analysed with a scanning electron microscope (SEM, Philips XL 30, FEI Company, Eindhoven, The Netherlands). The chemical composition on the surface of the untreated nickel titanium wires was analysed with EDX (Genesis 4000, EDAX AMETEK GmbH, Taunusstein, Germany).

2.3. General experimental procedure

A first characterisation of the wires was made by recording the open-circuit potential of the wires in an electrolytic cell for two hours according to ISO 10271 in modified Fusayama saliva at 37°C. Subsequently, current densities versus polarisation potentials were measured to determine breakdown potentials. Next, static immersion tests in artificial saliva and lactic acid, dynamic immersion tests with 42 thermal cycles, 5000 mechanical cycles and combinations of both in artificial saliva were conducted. Each immersion test was executed for one week at a temperature of 37°C. A thermal cycle consisted of 10 min at 10°C, 10 min at 37°C, and 10 min at 50°C to simulate a full martensitic transformation due to temperature changes. A mechanical cycle was a deflection of 1 mm for the reference wires and up to 2.5 mm for the NiTi wires to provide a martensitic transformation without fracture of the wires. The thermal cycles should simulate the exposure of the wires to hot beverages or food and to cold drinks or icecream. The mechanical cycles were chosen to simulate the intraoral stresses during mastication. After the tests the corrosion media were analysed with the ICP-MS for dissolved nickel ions and surfaces of the corroded wires were examined in the SEM.

3. Results

An overview of the results of all analyses is given in Table III for comparison reasons.

TABLE III Summary of the results. Note that the nickel release is given in μg/cm^2

	Potential (mV (SCE))		Nickel ion release (μg/cm^2)				
Product	Open circuit	Breakdown	Static	LA	Thermal	Mechanical	Combined
Titanol Low Force	−95	250	1.9	8.5	1.3	3.6	1.7
Tensic	−60	330	0.4	1.8	2.6	7.0	10.3
Copper Ni-Ti	−20	930	0.0	0.1	0.6	3.5	9.5
Euro Arch	−166	1200	0.2	0.1	1.0	1.9	3.3
Neo Sentalloy	−144	690	0.0	1.0	0.5	0.3	2.9
Nitinol Classic	−133	490	0.1	0.3	0.6	2.4	0.5
Nitinol Superelastic	−160	1470	0.0	0.3	0.7	0.2	2.3
Remaloy	−180	880	0.3	0.3	0.0	3.3	10.6
Noninium	−85	550	0.0	0.0	0.8	0.0	2.4
Rematitan Special	87	>2000	0.2*	0.0	0.5*	0.5*	0.5*
Remanium	116	690	0.3	0.1	1.2	0.4	4.1
Stainless Steel	124	590	0.0	0.0	0.6	0.2	0.4

*Doubly ionised 120-Sn.

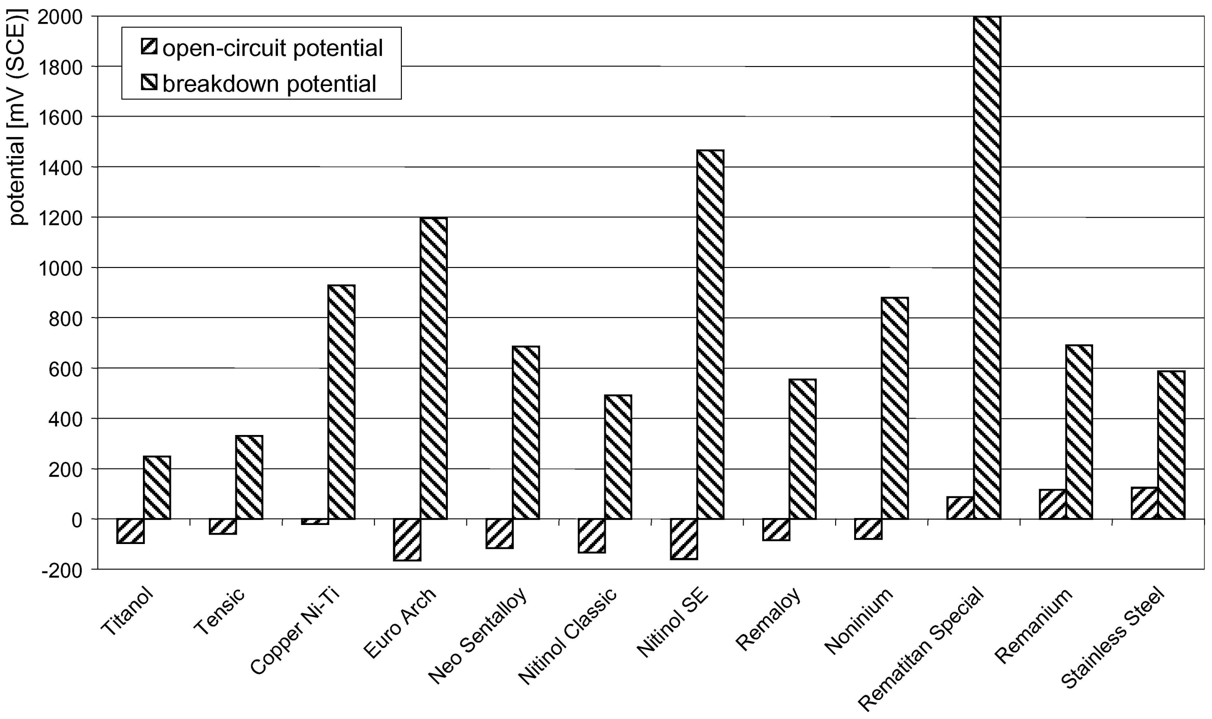

Figure 2 Results of the electrochemical test. Potentials are given in Saturated Calomel Electrode (SCE) Volts.

3.1. Breakdown potentials

Fig. 2 shows the electrochemical results. The breakdown potential of the titanium molybdenum wire could not be determined, as the working range of the potentiostate used was limited to ±2000 mV. All other breakdown potentials were within the working range of the setup. The nickel titanium wires did not show a uniform behavior although the chemical composition as shown in Table I is quite similar. Several wires had a very low breakdown potential (Titanol Low Force: 250 mV and Tensic: 330 mV) while others had significantly higher values of up to 1470 mV (Copper Ni-Ti, Euro Arch, Nitinol Superelastic). The reference wires had intermediate potentials (590–880 mV, see Table III).

3.2. Static immersion tests in artificial saliva and lactic acid

For the analysis of the nickel ion release in the immersion tests the nickel isotope 60-Ni was measured with the mass spectrometer in the corrosion media. 58-Ni has higher natural abundance but it coincides with 58-Fe. The respective Ni concentration determined was scaled to the total Ni release of the wires in the one week immersion tests and then converted into μg/cm^2 to determine the release per wire surface. The obtained results for all immersion tests can be taken from Table III. They vary from 0.1 to 8.5 μg/cm^2 for the different wires. In the static immersion tests in AS as well as in LA two wires (Titanol Low Force and Tensic) had clearly higher values for nickel release than the others (see Fig. 3). At the same time these wires have the lowest breakdown potential. The other wires display a nickel ion release of around 0.3 μg/cm^2, which in general is higher in LA. Although the TMA wire does not contain any nickel, a very low Ni release (up to 0.5 μg/cm^2) was measured for that wire. In fact TMA contains a several amount of 120-Sn and as the mass spectrometer detects a certain ratio of mass per charge, the measured nickel ion release of that wire was doubly ionised Sn.

3.3. Immersion tests with thermal and mechanical loading

Fig. 4 shows the results of the immersion tests combined with thermal and mechanical loading. In contrast to Fig. 3 and Table III the Ni ion release here is scaled to a daily ion release for a full mouth appliance. Three facts can be seen from this bar graph: (1) Thermal, mechanical and combined thermal/mechanical loading increases Ni ion release from NiTi orthodontic wires in the immersion tests. (2) The differences in Ni ion release among the wires is leveled by the loading. (3) Ni ion release from NiTi orthodontic wires with and/or without loading is in the same order of magnitude as Ni ion release from the reference wires, i.e. it ranges from about 1 μg/day to 8 μg/day. The only exception is the titanium molybdenum wire, that does not contain nickel and seems to release only a minor amount of 120-Sn.

The above-mentioned items (1) and (2) lead to the assumption that surface effects could play a major role in the different behaviours of the wires in the pure static immersion tests. In pure immersion tests, Ni release seems to be dominated by the surface of the wires, while in the immersion test with mechanical or thermal loading the behaviour of the bulk material becomes more and more important. Especially the application of mechanical loads in combination with thermal loading seems to increase the release of bulk ions. The wires Titanol Low Force and Nitinol Classic are an exception. Nickel release under thermal and mechanical loading is decreased rather than increased compared with the static immersion test in artficial saliva or the

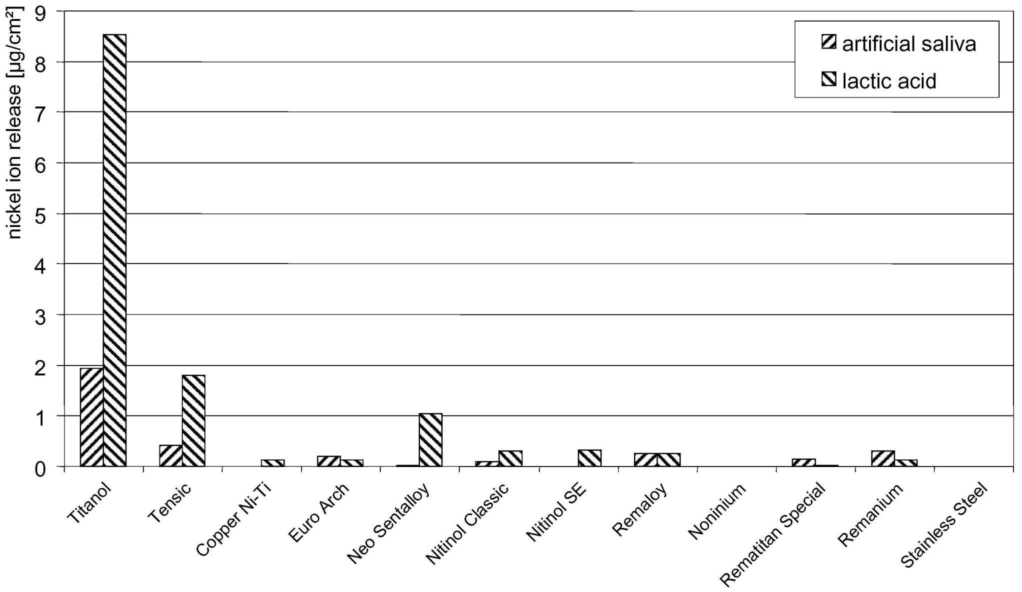

Figure 3 Static immersion test results. Nickel ion release after one week.

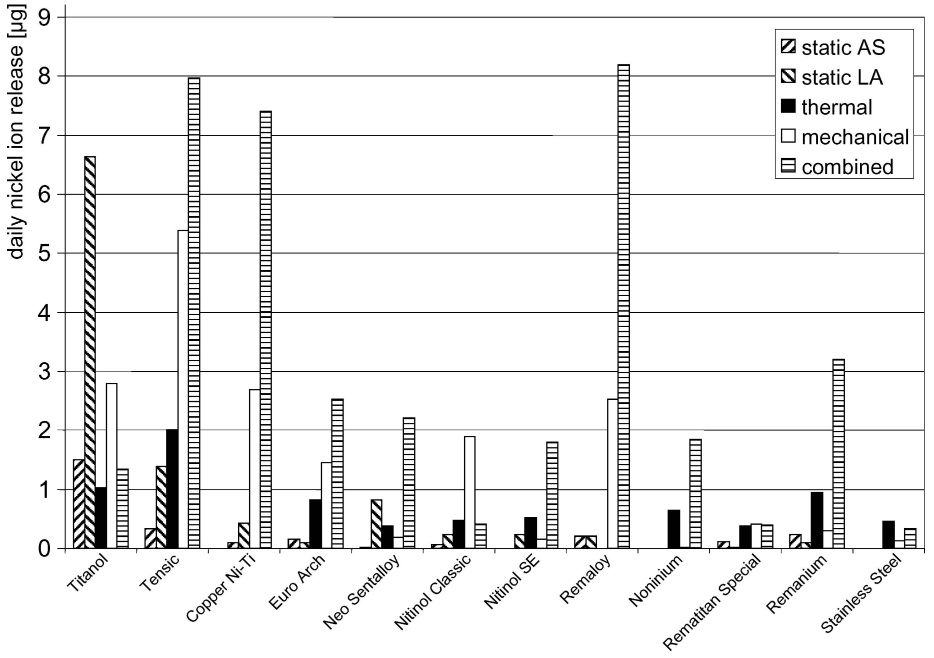

Figure 4 Immersion test results converted into daily nickel ion release, a total wire length of 28 cm is considered (upper and lower arch).

immersion test with pure mechanical loading. This behaviour might be explained with the experimental conditions which is discussed below.

3.4. SEM analysis of the exposed wires

Surface analysis of the wires after exposition in the corrosion liquids and provoked corrosion in the electrochemical cell is shown exemplary aid of the scans of the wire Tensic. The reference wire displays the typical surface structure of a NiTi wire (Fig. 5a). After electrochemical polarization most wires displayed extreme surface defects similar to that shown in Fig. 5b. In the immersion tests, static as well as combined with thermal or mechanical load, such defects could not be identified (Fig. 5c). Even the wire Titanol Low Force did not show any damage on the surfaces.

3.5. EDX analysis

Based on the lower breakdown potentials and the higher nickel ion release in the pure static immersion tests of the wires Tensic and Titanol Low Force it was assumed that surface effects play the major role in defining the corrosion behaviour of a wire. Therefore, the nickel titanium wires were analysed with energy dispersive X-ray analysis (EDX). All wires were fractured and the chemical composition on the fractured surface was compared with the outer wire surface. Figs 6 and 7 show SEM pictures of the wire Neo Sentalloy from the outer surface and the fracture surface. The surfaces of the wires looked all different due to different manufacturing processes. However, all fracture surfaces showed a similar kind of texture, as shown in Fig. 7.

The EDX spectra were integrated over the complete pictures each. The chemical compositions derived from

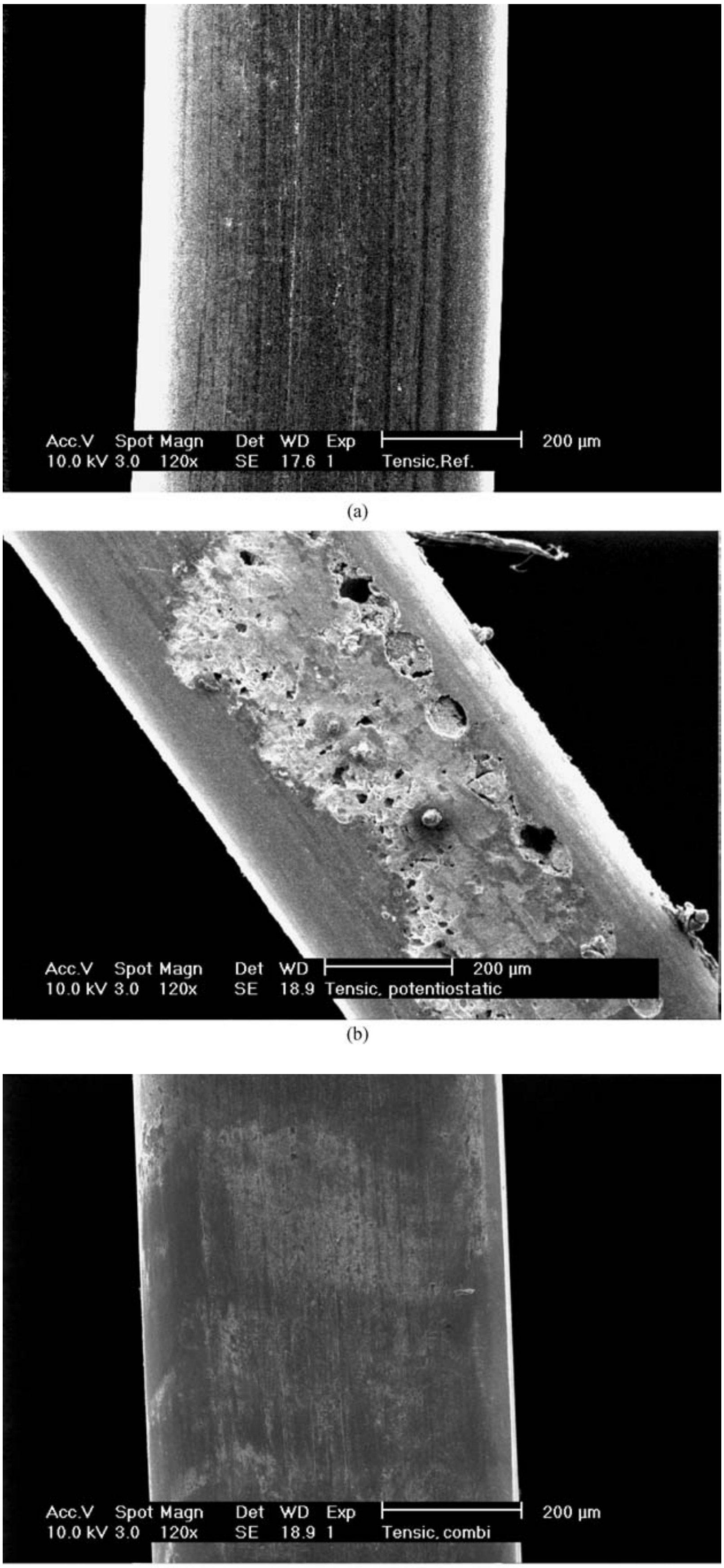

Figure 5 (a) SEM picture of the Tensic reference wire. (b) SEM picture of the electrochemically corroded Tensic wire. (c) SEM picture of the Tensic wire after combined thermal and mechanical loading.

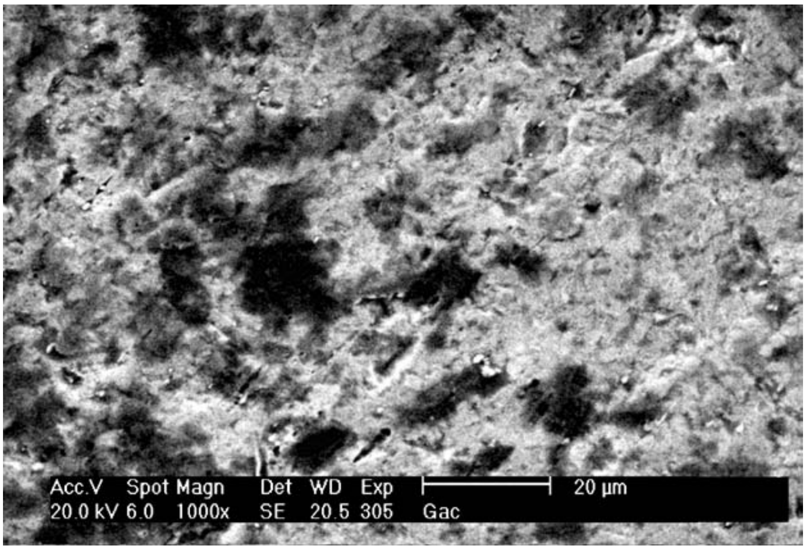

Figure 6 SEM picture of the Neo Sentalloy surface. The surface of all wires is not smooth due to mechanical processing during manufacturing.

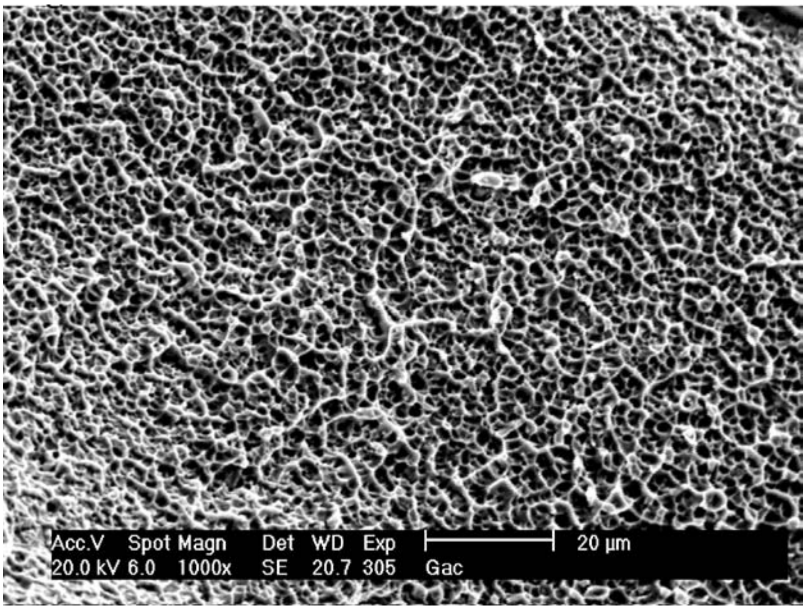

Figure 7 SEM picture of the Neo Sentalloy fracture surface. All NiTi wires show a very similar fracture surface structure and chemical composition.

these spectra are shown in Fig. 8. It is a section enlargement of the full bar graph starting at 0% and ending at 100%. It can be seen that the fracture surfaces of the wires have a similar chemical composition of about 51.8 at% nickel and 48.2 at% of titanium under the assumption that copper in the Copper Ni-Ti belongs to the nickel part. The Nitinol Classic has a lower value of 50.9 at% nickel on the surface as well as in the bulk. With that alloy composition, this wire is not superelastic at the given temperature of 37°C. The Titanol Low Force has more than 5.0 at% of aluminium on its surface, while the composition of the Tensic wire at its surface comprises almost 59 at% of nickel. Both findings seem to have a negative influence on the corrosion behaviour of these wires. This is levelled by thermal and/or mechanical stress, as then the behaviour of the wire surface becomes less important than the corrosion behaviour of the bulk material.

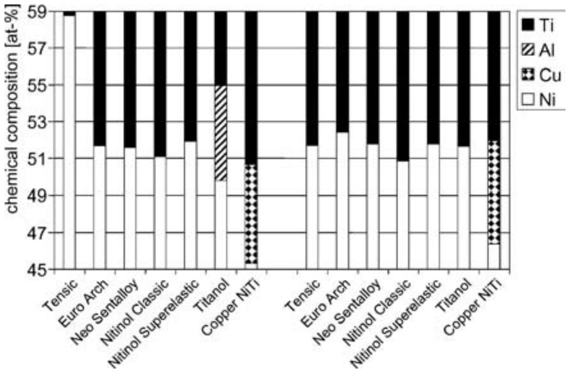

Figure 8 EDX analysis of the chemical composition of the NiTi-wires. On the left are the outer surface and on the right the fracture surface compositions.

4. Discussion

The above presented results have to be discussed with respect to aspects of biocompatibility. First, the values of the nickel release have to be converted into the more interesting unit μg/day, see Fig. 4. In that calculation, a total wire length of 28 cm for an orthodontic appliance (upper and lower arch) was considered and consequently the surface was estimated to be 5.43 cm^2. Determination of the nickel release for one day requires division of the ion release by 7, even though one could expect that most nickel will be released during the first couple of days. The maximum of nickel release in Table III is given to be 10.6 μg/cm^2 corresponding to 8.2 μg/day. This is almost two orders of magnitude below the daily dietary intake level (300–500 μg) [21] and the critical concentration (600–2500 μg) necessary to induce Ni allergy [22]. The values match with a study [23] in which different nickel titanium wires in the same modified Fusayama saliva were used with added lactic acid at a pH level of 2.5. The converted maximum value reported therein was 16.8 μg/day for a full mouth appliance.

The electrochemical tests are in good agreement with previous results [24, 25]. These earlier studies focused on the determination of the break-down potential of orthodontic wires and their corrosion behaviour under potentiostatic loading. In the present study, this corrosion behaviour in electrochemical testing was interconnected with the results in static immersion testing, including mechanical and thermal loading of the wires, in order to determine the clinical relevance of the previously determined electrochemical results. It can be seen that the orthodontic NiTi wires display differences in their corrosion behaviour in electrochemical tests. Two of the wires, that are Tensic and Titanol Low Force, had the lowest breakdown potential and at the same time the highest nickel release in the static immersion tests in artificial saliva and lactic acid. But, this behaviour must be seen with respect to their chemical surface composition. The Tensic wire contains an excess of nickel at the surface that is probably not bonded to the titanium. Thus nickel can easily be released. The Titanol Low Force contains aluminium on the surface, probably originating from the polishing agent and supporting the nickel release. On the other hand, the copper in the Copper Ni-Ti does not seem to have any influence on the corrosion behaviour.

The results in the dynamic immersion tests are inconsistent although it could be expected that combined loading always results in higher nickel ion release than the pure mechanical test. Three items have to be discussed with respect to these results: (1) The basic problem concerns the adjustment of the mechanical loading device. The wires have to be displaced so far that they transform to the martensite. The exact deflection necessary for that is quite difficult to determine, and it differs extremely from wire to wire. Additionally, the loading device of the machine could be adjusted with an accuracy of approximately 0.1 mm. Together with the uncertainty of the deflection to be adjusted, this might have influenced the nickel ion release of the individual wires. (2) Moreover, the nickel ion concentration in the corrosion liquids was very low, as generally few ions were released into a relatively high volume of corrosion liquid. Partially, the Ni concentration was near to the detection limit of the ICP-MS. 3) The third item has to be seen in common with that. The immersion tests were extremely time consuming, each test did last one week, resulting in a total of 36 weeks for the dynamic test of all wires. Consequently, it was impossible to perform a series of tests for each wire and experiment. Instead, ten wires were loaded simultaneously and thus, a statistical analysis seemed to be inappropriate.

Nevertheless it can be seen that the nickel release of all wires seems to be balanced by mechanical and thermal loading. The highest ion release determined for three wires in the combined mechanical/thermal immersion test reaches about 8.0 μg/day, the lowest 0.5 μg/day. So, nickel release from the Remaloy wire is in the same range as that from the NiTi wires, while the values determined for Rematitan Special and Stainless Steel are lower. All values are far below the daily dietary intake level.

5. Conclusions

Nickel titanium seems to be a biocompatible material and is applicable for orthodontic treatment. Even under mechanical and thermal loading the nickel release is far below the daily dietary intake level. The release of nickel can be reduced if the surface nickel concentration is in the same range as in the bulk of the superelastic material. The presence of aluminium on the surface seems to have negative influence on nickel ion release as well, while nickel substitution by copper is neutral. The breakdown potential test and the EDX analyses are fast and easy to use methods to determine whether the surfaces of nickel titanium wires are optimal with respect to nickel ion release.

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