

Degradation of lingual orthodontics archwires

The effect of corrosion and nickel release on their properties

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Discussion

4.1 Open circuit potential results

As it can be observed, OCP results are relatively difficult to compare due to the variation that exists among the specimens of the same material as shown at the graphs presented at the results chapter.

Although OCP is sometimes difficult to stabilise, it seems that after three hours of testing time, the curves showed a good enough stabilisation trend so to be able to set the final value as the starting point for the cyclic voltammetry. The exception seems to be the D-Rect archwire labelled as 2. As it can be seen at the graph, the archwire seems to need a bit more of time in order to assert that a stabilisation trend was achieved.

All archwires were measured under the same conditions so OCP variations seem only to be due to the specimen. Variations introduced at the manufacturing processes may be responsible of it.

As it was seen at the results chapter, wires could be classified into three groups according to the OCP behavior:

1. The braided wires and the 0.016 stainless steel.
2. The 0.016x0.022 stainless steel.
3. Titanium alloys group.

The first group showed similar OCP records whose values can be seen to be around -400 mV and -580 mV.

The 0.016x0.022 ss group kept the OCP values roughly under -332 mV and above the -400 mV threshold.

The third group showed very variable OCP results. At the negative values TMA reached a lower value of -286 mV very closely followed by similar values of NiTi and CuNiTi archwires. Positive OCP results ranged from 123 mV to 270 mV.

Surface variations have a great deal to do with variability in the OCP test. Slight changes in surface due to manufacturing processes or surface defects can vary the potential in several hundreds of units so the results obtained are not that surprising.

It is known that the scanning rate that it is chosen when performing an OCP could lead to variability in the obtained results as some studies conclude¹⁴⁴⁻¹⁴⁸. The OCP at the test was always done for 3 hours with measures taken every two seconds, so the scan rate in the measurements was always the same and can not be a factor to account for OCP variability.

It is also known that prolonged times of OCP testing can lead to a variability in the results obtained. Schiff et al¹⁰ compared OCP of different wire materials in different kinds of fluoridated mouthwashes. Their study is conceptually misleading at the first experimental measurement. They performed an OCP but they labeled the results as E_{corr} when OCP was looked for. Anyway, their results allow proving the fact that prolonged OCP's could lead to different results. If attention is focused on studies performed on Fusayama artificial saliva preparation it could be seen that there is a slight variation of the OCP obtained although the potential could appear to be stabilized at any point. The results obtained after 24 h of OCP testing were:

TMA= -280 mV

NiTi= -150 mV

CuNiTi= -140 mV

(in mV/SCE)

The aeration conditions of the electrolyte could lead to a variability of OCP results as Mangin et al¹⁴⁹ state. At the present laboratory setting this issue was not controlled in a specific manner. The electrolyte was simply on a glass container whose temperature was controlled by the surrounding bath of water at 37°C. There was not an aeration control by means of a gas bubbling. The cell had a mechanic vibration system that avoided the concentration gradients of the electrolyte which has been sometimes pointed out as a factor influencing the OCP results. In fact this is regulated at the ISO 10993-15:2000. Although any of the systems might be present, it is always very risky to say that the gradient is always homogeneous, so it is always better to assume that OCP can in the end be influenced by it.

Other studies point out the immersion time prior to the test of the specimen as a factor that modifies OCP results^{148,150}. At the present test this could also be considered a factor to be taken into account. The cleaning process in order to prepare the specimens was not done in an

exact manner. Distilled water cleaning was always done for a short period of time, around thirty seconds, and ultrasonic cleaning of the specimen was usually done for 4 minutes.

Geometry is sometimes said to be a factor related to variation in OCP measurements¹⁵¹. It is an obvious factor when different specimens are compared specially at the wire sequences tested at this experimentation. In any case, the compared changes that are being studied are not inter wires but intra wires. There are significant changes among wires that have the same macroscopic geometry. It would be easier to understand that this factor influences more the braided wires than the rest. Braided wires are formed of small winded wires that not always may lead to the same surface to be exposed to the electrolyte. A round cross-sectional braided wire can be expected to be more regular in surface for a given length than a squared braided wire like the D-Rect. As it can be seen at the low augmented scan views of the SEM, the edges of the D-Rect wire show a surface variation that is difficult to control at the manufacturing process. Therefore OCP variation should be expected at these wires as it really turns out to be.

What it seems to account for the OCP variability results among arches of the same material is the surface finish of the sample^{150,152-156}.

Most studies that refer to corrosion in orthodontics used SEM as one of the methods of assessing the specimens under study prior to the corrosion testing and, also obviously after in order to evaluate the microscopic changes. Most of them agree that surface defects are regularly present at most orthodontic archwires^{7-17,20,22-25,28,29,138,157}. Many of them have manufacturing defects on the surface at the as-received state.

As it can be seen at the pictures taken at the SEM, the as-received wires show several indentations and grooves resulting from the drawing and rolling of the manufacturing processes. The braided wires, due to the fact of being made of several wires, have an increased probability of presenting more manufacturing defects than a single body wire. This would help explain the OCP variation of the braided wires among different specimens.

Besides the defects that might be present, the surface finishing has a great deal to do with OCP variations of the archwires of the same material. Alonso-Falleiros and Wolyne¹⁵⁸ studied the corrosion potential and its correlation with the pitting potential and they reached several interesting conclusions that help understand the OCP results variation at the test. One of the conclusions they reached was that OCP and the standard deviations at the results of their study were strongly affected by the type of surface finish. Their OCP values changed severely depending on the surface finishing of the metal tested by hundreds of mV. Even at the groups of metals

treated at their surface with the same method, a standard deviation of hundreds of mV could be found.

The specimens of the lingual archwires submitted to OCP testing were not superficially modified by grinding or polishing, they were just cleaned with a standard protocol previous to the test. OCP variation was not to be studied per se, if so a surface treatment would have been performed in order to achieve a regular surface for all of them. But as Alonso-Falleiros and Wolyneć¹⁵⁸ show, this would have not spared the variability found at the OCP.

In any case, the OCP testing of the lingual archwires as well as the rest of the experimental set up, aims to describe the properties of the archwires as-received from the manufacturer and not in a prepared way that would not be done on a clinical scenario.

Prior surface treatments of the wires resulting from manufacturing are unknown and remain undisclosed by the manufacturers so any efforts regarding the understanding of OCP variability are a merely approach to supposed causes.

As some authors state³², the fulfillment of the manufacturing requirements according to the ISO and therefore by the Comité Européen de Normalisation and the American Dental Association are not still a must. Manufacturers can formulate their own standards and a lot of wires can differ from the next one. The authors mentioned that information regarding manufacturing processes like drawing, reduction per pass, number of passes, lubrication materials and heat treatments is proprietary of each manufacturer and it remains undisclosed for being an industrial secret.

This information would be of great help in order to understand the changes of properties of wires of the same material. A simple example illustrates how changes in surface do occur: there have been different authors that have studied the variations of dimensions of archwires and brackets and have found them to be smaller or bigger than the manufacturers' statement of sizes^{110,128,159,160}. This is an example of the lack of control in the manufacturing processes that due to an inexistent manufacturing regulation allows orthodontic products to be at the market place with a range of variability in the properties.

From the results obtained at the OCP and considering that generally speaking the higher the value at which the material gets its stabilization potential the more resistant to corrosion the material will be it could be concluded that:

1. Titanium alloys of the lingual archwires studied showed the highest OCP values so they are more resistant to corrosion than the rest of the archwires of the sequence of arches tested.
2. Stainless Steel 0.016x0.022 archwires showed a slightly higher corrosion resistance than the rest of stainless steel wires of the lingual series tested, being its OCP under -400 mV.
3. The braided wires Respond and D-Rect and the stainless steel 0.016 wire showed the lowest OCP values being therefore more prone to corrosion with similar values in all of them.
4. According to the scientific literature and what the SEM scans of the as-received lingual archwires show, surface finishing may be responsible of the OCP variability found, specially among the wires which are less resistant to corrosion.

4.2 Cyclic Voltammetry results

The graphs that depict the whole cyclic voltammetry testing show very similar behaviors for the archwires of the same group. It could even be said that all the stainless steel archwires could be considered the same group given that their cyclic voltammetry tests are very similar. The rest of the archwires behave differently to each other.

The aim of the test is studying the point at which rupture potentials (breaking potentials or pitting potentials) start taking place. It will always be at the anodic area that is delimited by the OCP value for a given specimen. Rupture potentials indicate the potential at which pitting is starting, most times as pit defects on the surface of the material.

Cyclic Voltammetry started at the OCP values found at the OCP testing. The potentiostat scanned the current density variation by increasing or decreasing the potential at a rate of 0,25 mV/s. For most of the lingual archwires, the potentiostat was programmed to scan 300 mV under the OCP value and up to 2000 mV above it with the exception of the TMA specimens that due to their resistance were scanned up to 2700 mV above the OCP. The materials and methods chapter describes the methodology followed.

In contrast with the OCP testing, results among specimens of the same material were found to be very consistent.

General graphs shown at the results chapter had the potential (mV) plotted against the current density (mA/cm²) of the specimens tested after the OCP test had finished.

Besides defining the breakdown potential (E_b) for each material that establishes the point at which the material starts pitting, cyclic voltammetry results allows comparisons among different materials in order to determine which one corrodes more easily. This point is labeled E_{corr} as it was previously said.

The fact of plotting the potential against the log (i) helps obtaining very clear peaks that help localize E_{corr} and so I_{corr} which is the current that flows at E_{corr} and obtain another way of checking E_b .

I_{corr} is very useful when predicting the rate of corrosion of the material.

Log plots are also useful for another reason. When the potential of the corroding material is carefully displaced by the potentiostat away from E_{corr} there is a region of 10 mV around it where a linear relationship between the potential and the current holds. The slope of the linear polarization curve dE/di is called polarization resistance (R_p) which is inversely proportional to the rate of corrosion.

According to the graphs obtained from the cyclic voltammetry tests the log i graphs are shown at graphs from 40 to 46. From their study, the following E_{corr} could be obtained:

Respond: -600 mV (graph 41)

D-Rect: -650 mV (graph 42)

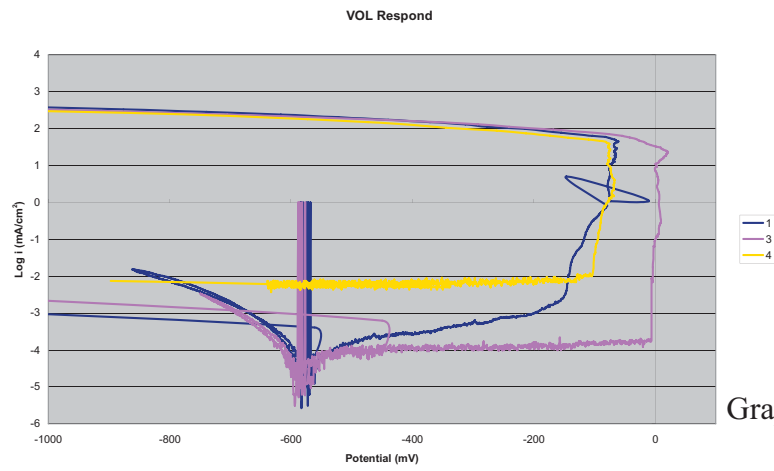
Stainless Steel 0.016x0.022: -610 mV (graph 43)

Stainless Steel 0.016: -845 mV (graph 44)

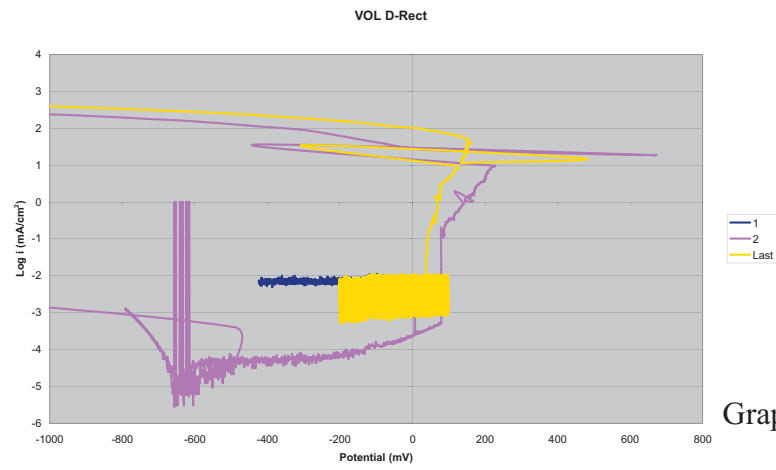
NiTi: 1000 mV (graph 45)

CuNiTi: 1000 mV (graph 46)

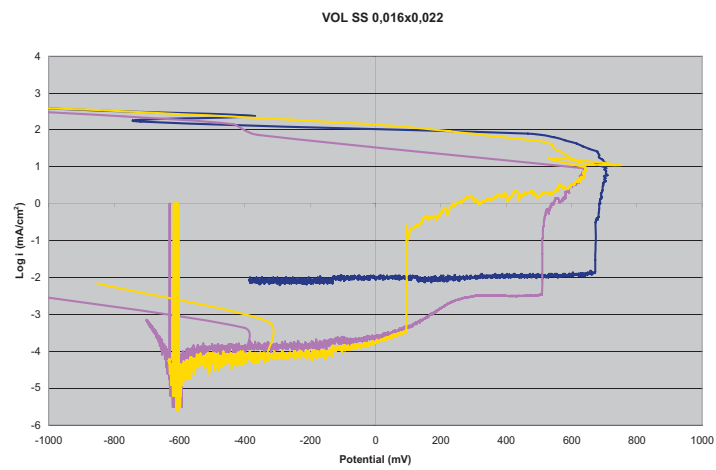
TMA: 1000 mV (graph 47)



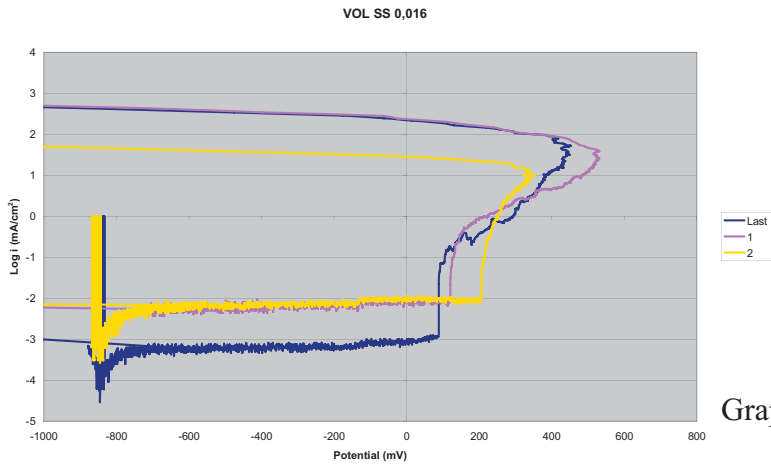
Graph 41



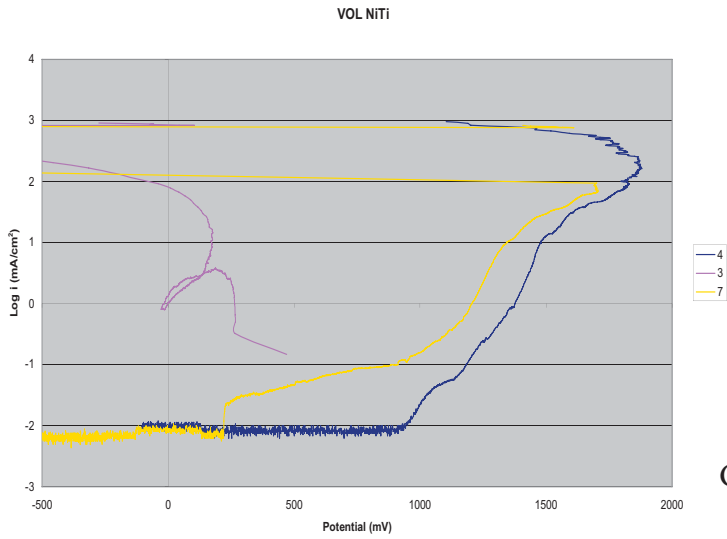
Graph 42



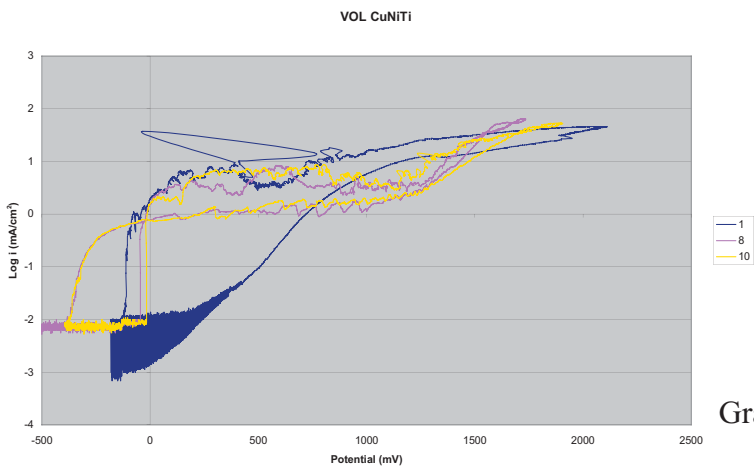
Graph 43



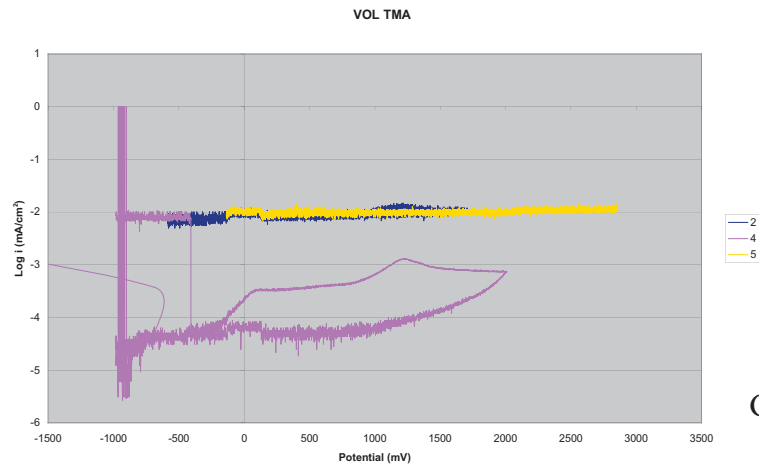
Graph 44



Graph 45



Graph 46



Graph 47

Results found for the Respond archwires are very similar (graph 41). Specimens 1 and 3 got very similar E_{corr} measurements that peak around -600 mV. Their i_{corr} could be estimated to be around -4 and $-4,5$ mA/cm². The polarization resistance seems to be also very similar for both. As it can be seen from the graph, the current at the anodic reaction reaches a maximum and then it decreases to a smaller value. At the specimens tested this fact occurs around -148 mV for specimen 1 and around -6 mV for specimen 3 and -103 mV for specimen 4. This point indicates the moment at which an oxide thin film has formed and spread over the surface of the specimen. The flow of metal ions through the oxide film becomes slower and so current density due to metal ions leaving the metal decreases becoming smaller and smaller as the oxide film grows. This is known as the passivating of the metal. Then at the point E_b described at the results chapter, pitting starts occurring and the passive layer of oxide disrupts. Respond wires showed pitting between -75 mV and 10 mV.

D-Rect cyclic voltammetry shows incomplete results (graph 42). Out of the five tested specimens at the OCP, only three of them completed the cyclic voltammetry test. Out of the three specimens that passed on to the CV, only specimen 2 seems to show the cathodic to anodic transition point where E_{corr} and i_{corr} can be estimated. Therefore, it seems that the OCP values for specimens 1 and last did not yield a stabilized OCP value. According to the obtained results, E_{corr} was around -650 mV and i_{corr} could be estimated to be around -4 and $-4,5$ mA/cm². The polarization resistance seems to be very similar to the obtained for the Respond archwires. Pitting information can be obtained from the three specimens and their E_b is confirmed by the log plots to be between 41 mV and 79 mV.

CV results found for the Stainless Steel 0.016x0.022 archwires were also very similar (graph 43). Specimens 3 and 4 got very similar E_{corr} measurements that peak around -600 mV. Specimen

1 did not show a cathodic to anodic transition. This fact may be due to the lack of stabilization at the OCP testing. The i_{corr} could be estimated to be around -4 and -4,5 mA/cm². The polarization resistance seems to be also very similar for both. These wires showed pitting between 95 mV and 673 mV.

The Stainless Steel 0.016 archwires are very similar (graph 44). Specimens Last and 2 got very similar E_{corr} measurements that peak around -845 mV. Their i_{corr} could be estimated to be around -3 and -3,5 mA/cm². The polarization resistance seems to be also very similar for both. E_b were found to be between 90 mV and 205 mV.

NiTi archwires show also a similar trend at their group (graph 45). The log plot is not as clear as the stainless steel wires and is difficult to analyze as the CuNiTi CV results. Specimen 3 seems to be incorrect and should be discarded for CV analysis. Specimens 4 and 7 got very similar E_{corr} measurements that peak around 1000 mV but still this peak is unclear. Their i_{corr} could be estimated to be above -2 mA/cm², but nothing else can be said according to the obtained data. The polarization resistance seems to be also very similar for both. E_b described at the results chapter differs from the obtained at the log plot in which the values for specimens 4 and 7 seem to be 1850 mV and 1700 respectively.

CuNiTi archwires results do not yield the typical shape for the cathodic to anodic transition graph (graph 46). All specimens showed a complete back and forward CV test line. E_{corr} seem to be around 1000 mV for the three specimens. Their i_{corr} could be estimated to be around -2 mA/cm². The polarization resistance seems to be also very similar for all. E_b starts occurring between 600 mV and 1187 mV.

Finally, TMA results are difficult to analyse (graph 47). E_{corr} measurements could be obtained from specimen 4 that peak around 1000 mV. Their i_{corr} could be estimated to be around -4,5 and -5 mA/cm². The polarization resistance can not be really determined given that the graph is unclear and a line can not be really drawn seems to be also very similar for both. Point E_b described for this specimen is 2000 mV. This seems to be clearer at the log plotting that at the initial results presented at the results chapter. These wires were found to be highly resistant to anodic polarization and so the fact of being unable to get clearer graphs for the CV testing of this material was not a surprising outcome.

E_{corr} , i_{corr} and E_b measurements seem to be more consistent than the OCP measurements. Stainless Steel, braided wires included, show reproducible results. These results are valid for a rough comparison with results obtained by other authors with archwires of the same material used

in vestibular orthodontics. TMA results show that the material is highly resistant to corrosion and NiTi showed the highest breaking potentials of all the lingual archwires tested.

Not many authors address the topic of breaking potentials in orthodontic wires.

Neumann, Bourael and Jäger¹³ studied conventional orthodontics NiTi archwires of the same dimensions and their findings could not be more astonishing. The composition of the archwires did not differ significantly but the surface treatment or coating was different for the wires being uncoated, polished, polyethylene coated, teflon coated and ion implanted. It seems that results were very influenced by the surface properties.

Results adapted from the authors¹³ regarding the E_b are shown in table 17.

Wire	Surface/coating	Potential (mV/NHE)
Bioforce Sentalloy (GAC)	uncoated	460
Bioforce Sentalloy longuard (GAC)	ion implanted	600
Rematitan Lite Dimple (Dentaurum)	uncoated	190
Titanol River Finish (Forestadent)	uncoated, polished	350
Titanol River Finish Gold (Forestadent)	polyethylene	340
Titanol River Finish Gold 2 (Forestadent)	polyethylene	260

Table 17

It is noticeable the variability that they found among archwires of the same material. E_b ranged from 190 mV to 600 mV when a reference versus a NHE is used although the reference electrode used by the authors of the study was a Ag/AgCl reference electrode (Type B 2820, Schott, Germany) which is similar to the one used at the present experimentation. It should be kept in mind that the Ag/AgCl electrode used at the E_b testing of the lingual archwires was $E^0=0,222$ V for conversion purposes.

In any case, conversion of units does not add up any new conclusion given that variability remains constant at their study. Variability shown in E_b found by Neumann, Bourael and Jäger¹³ is clear even in wires whose surface was “equally” treated. If Neumann et al¹³ results are transformed for the Ag/AgCl values and are then compared to the results obtained at the present experimentation, it could be concluded that breaking potentials found for the lingual NiTi wires are at least 1000 mV above. There is a weak point at the study by Neumann et al¹³. The specimens were only polarized for 10 minutes. This is a very small amount of time compared to the cyclic

voltammetry test performed at the lingual archwires at the present research. A different electrolyte was also used but this should not make the difference that big.

An interesting finding was reached by Neumann et al¹³ that coincides with the present experimentation. As they state, TMA breaking potentials could not be determined as expected initially given their high resistance to corrosion. This behavior is explained by the use of the highly corrosion resistant β -Titanium alloy and not by the surface modification done by the implantation of ions to which the studied wires were submitted to. Lingual TMA wires were not found to be corroded or affected by the CV test at the present experimentation, so this is in agreement with Neumann et al¹³ results.

A study by Widu et al¹⁴ that also dealt with breaking potentials reached similar results for NiTi wires. Four groups on different NiTi were tested, a TMA and a stainless steel archwire was also tested. Table 18 shows the results adapted from the authors.

Wire	E_b (mV/NHE)
Titanium memory (American Orthodontics)	320-370
Neo Sentalloy (GAC)	370-420
Ni-Ti (Ormco)	720-770
Nitinol (3M Unitek)	720-770
TMA (Ormco)	
Stainless Steel (3M Unitek)	620-670

Table 18

There seems to be even a shorter polarization at these specimens, they were only polarized for 1 minute. The electrolyte was a Fusayama-Meyer preparation and a Ag/AgCl electrode was used.

Kim et al²⁴ obtained the results shown at table 19 (adapted from the authors) when breaking potentials were analyzed.

Wire	E_b (mV/SCE)
Stainless Steel ("A"-Company)	400
NiTi-A (FlexMedics)	300
NiTi-B (Ormco)	750
NiTi nitride coated (FlexMedics)	300
NiTi epoxy coated (FlexMedics)	1800
TMA (Ormco)	not found up to 2000 mV

Table 19

Once again, results are hardly comparable. Again TMA showed a high corrosion resistance and no breaking potentials were recorded, being for the authors chemically inert. Breaking potentials found for the stainless steel wires tested were quite similar to the obtained for the stainless steel 0.016x0.022 lingual wires at the present experimentation. But comparisons between both studies are not possible given the different experimentation set-ups and the materials and methods used.

Although comparisons can not be established easily, these studies lead to a point that has been thoroughly contrasted at several scientific research articles: the variability in breaking potentials results.

Some authors reached the conclusion that NiTi alloys exhibit a wide passivity range that goes up to high potential values that would not be found in fluids of the human body. Speck and Fraker¹⁶¹ and a study by Sedriks et al¹⁶² found values ranging from 1100 mV to 1300 mV. When dealing with Ti wires, Speck and Fraker¹⁶¹ found breakdown potentials around 2000 mV. Similar results were found by Rondelli et al¹⁶³ whose breaking potentials for NiTi were found to be around 1200 mV versus SCE ($E^{\circ}=0,24$ V). Other authors have reached conclusions that underscore the breaking potentials previously found. Lower resistance of NiTi in comparison with Ti alloys was found by Edie et al²⁵ when comparing pitting corrosion. Other studies also found low pitting resistance in NiTi alloys^{164,165}.

At the present study, when dealing with the OCP results for NiTi lingual wires, it was seen that there was a high variability. One of the three NiTi lingual wires tested showed very different CV results from the other two. Being an alloy with such a good behavior against corrosion it still shows high variability.

This fact would be explained by some of the conclusions reached by Kimura et al¹⁶⁶. They found that although the range of passivity of the alloy is generally satisfactory some of the tested specimens yielded low breakdown potential records. This is the same conclusion that Nakayama et al¹⁶⁷ reached. They found certain variability in pitting potential values in both in vivo and in vitro potentiodynamic tests that were considered to be due to the variability of the properties of the passive film present on the Ni-Ti alloys.

As it was explained at the materials and methods chapter, the NiTi passive film consists of TiO_2 mainly but, according to some authors^{165,166} the melting process in graphite crucibles results in the presence of carbides on the specimens surface. As it has been tested these carbides can destabilize locally the passive film becoming the precursors of the pitting defects' onset¹⁶⁵.

NiTi surface modifications in any of the possible ways has been proven to be a factor that renders a high variability in the breaking potentials results as tested by the several authors^{94,166,168}.

Rondelli et al²³ also think that any defect that locally affects the passive film by scratching disrupts it in such a way that the reconstruction of the film is a relatively difficult process as the ASTM F746 test shows²³. Their findings are quite clear with regards to the role that scratches play in the breakdown potentials. When potentiodynamic tests were performed in an isotonic saline solution (0,9% NaCl) pitting potential values decreased with respect to the artificial saliva preparation. They state that by comparing them with the range of potentials that titanium and stainless steels attain in vivo, these materials should be considered susceptible to pitting. In fact the ASTM F746 test showed even lower localized corrosion potentials. When testing was done on artificial saliva preparations, generally no pitting occurred up to high potentials.

Contrasting the methodology followed by Rondelli et al at their study²³ with the present experimentation, it should be said, that the use of a HBSS gives a closer prediction to pitting values although differences might found to be greater if the wires have scratches on the surface due to manufacturing processes or due to the specimen preparation protocol. This is a reason that gives support to the fact of choosing HBSS instead of any of the possible artificial saliva preparations that are available at the market and that are vastly used in corrosion experimentation. Previous studies showed that potentiostatic anodic polarization results using physiologic saline solutions obtained comparable results to those performed in blood, extracellular fluids and saliva¹⁶⁹⁻¹⁷⁸.

Cross section geometry and shape does not seem to play an important role when it comes to compare pitting potentials among archwires of the same material as Rondelli et al²³ conclude. When 0.016x0.022 and 0.018x0.025; 0.016 and 0.016x0.022; 0.016 and 0.018x0.018 were compared, no significant changes in pitting potentials occurred.

At an earlier presented study by Kim et al²⁴, lower than average results were found for the breaking potentials of NiTi archwires. Curiously the experimentation set-up was very similar to the present experimentation set-up. Physiologic saline solution was used (0,9% NaCl) and aeration of the electrolyte was not controlled in any particular way. Even archwires were tested in an as-received state without being polished prior the anodic dissolution in an attempt to more closely simulate the clinical conditions although this could be in detriment of the reproducibility of results.

Although being similar studies, results are quite different. This brings us back again to the issue of the surface variation among wires. It could be stated that, on the overall, the NiTi and CuNiTi

archwires exhibit a very good behavior when compared to the NiTi archwires presented at the studies done by Neumann et al¹³, Widu et al¹⁴ and Kim et al²⁴. This could be due to the fact that, in general, they present less surface defects and irregularities, less phases of the metal are present and also there may be fewer differences in the corrosion cell environment (aeration-deaeration condition)

It has been shown that although higher breaking potential values have been found at the lingual orthodontics archwires experimentation, variability of results is also present as in any other experimentation. When comparing these results to those obtained by Speck and Fraker¹⁶¹, it is of great help recalling a statement made by them when comparing their results with previous experimentations. They said that when previous studies shown that samples which clearly exhibited irregularities at the surface prior to anodic polarization, breakdown potentials were found to drop as low as 430 mV.

A topic that still should be made clearer is that one regarding the experimental conditions of the electrolyte.

Although Fusayama-Meyer artificial saliva preparation or even the modified preparation of this electrolyte could have been used (or any other preparation of artificial saliva), the HBSS seems to be a better option due to the reason previously given according to Rondelli et al²³ findings and because it has been seen in many in vitro corrosion studies that the results obtained with these kind of saline solutions are comparable with studies performed in blood and any other extracellular media and that similar results were obtained when saliva was used.

Control of oxygen present at the electrolyte and the corrosion cell seems to have little or no impact on the final results. Kim et al²⁴ stated that their study was performed without purging the oxygen in an attempt to more closely simulate the oral environment. This is also the reason why at the testing of the lingual archwires it was decided to proceed in the same way.

At their experimentation, Sedriks et al¹⁶² found no significant differences in breakdown potentials when metals that were tested in an aerated solution were compared to metals under deaerated solutions at room temperature. Although no significant differences were found when comparing breakdown potentials, it was seen that the metals tested in aerated solutions exhibited a faster increase in current density and they reached at the end higher current densities.

Temperature variations do not seem to have a big impact on breakdown potentials variability. Speck and Fraker¹⁶¹ did their experimentation at body temperature (37°C) and the breakdown

potentials obtained were slightly lower than the obtained by Sedriks et al¹⁶² at room temperature. Breakdown potentials obtained at the present experimentation were noticeably higher than obtained by Speck and Fraker¹⁶¹ for NiTi even taking into account that they were also performed at body temperature (37°C). It does not seem to be a relation between temperature and breakdown potentials when the range of temperatures comprised between room and body temperature (37°C) is considered. Furthermore, if studies by Neumann et al¹³, Widu et al¹⁴, Rondelli et al²³ and Kim et al²⁴ are considered (temperatures ranging from room temperature to 40°C) there is no logic or relation to be found between both variables.

4.3 Photograph analysis

As it was seen at the results chapter, the area of contact between the braided wires that form the Respond wire is the very affected by polarization (photo 25). The analysis of photographs allows us only to assert that, from a macroscopic point of view, there is a big loss of material due to polarisation at the contact area of the wires that form the strand and this is most likely the result of a galvanic effect at that area. According to Iijima et al³¹ and to the common knowledge in electrochemistry, a galvanic cell is created when two different metals, or different areas on the same metal, are coupled.

This also applies for other braided wires, like the D-Rect used at the present study (photo 26). As it can be seen from the photographs, the areas where the biggest loss of material coincides with contact points of the wires that form the strand. This fact could be easily explained by the above introduced galvanic effect.

Non-braided stainless steel wires (0.016x0.022 and 0.016) show a high influence of polarization (photos 27 and 28 respectively). The squared section wire shows extensive pitting over the whole surface and a characteristic loss of metal at the edge that recalls a bite. This indentation is the result of the cumulative effect of pitting at the edge, point that is more severely affected by polarization. The 0.016 wire seems to be from the macroscopic point of view the wire that is the most affected by polarization out of all the wires of the lingual arches studied. It shows a very important loss of metal in an uneven fashion. Pitting corrosion, which is massive, leads to a modification of the section rendering it very irregular and losing completely the round section.

NiTi (photo 29) and CuNiTi (photo 30) wires show a good resistance to polarization. Both alloys keep their original shape round or squared respectively and polarization gives rise to a surface change. Corrosion leaves a rougher surface as it can be seen at the photographs and pitting is not present as it was seen at the stainless steels. It could be said that surface in both

wires suffers some kind of delamination. Surface corrodes leaving irregular defects that are clear especially at the CuNiTi wires. This is in agreement with some previous findings by Iijima et al¹⁷⁹. The authors reported that additions of 4,97% of Cu and 0,29% of Cr improved superelasticity properties of NiTi but did not improve the resistance to corrosion of the material. Their x-ray photoelectron spectroscopy study performed on CuNiTi specimens showed that metallic copper was enriched at the alloy/oxide film interface giving as a result an increased susceptibility to pitting corrosion. The results found at the present study are in agreement with those findings and are also in agreement with the results obtained by other authors⁷. There are some authors that have reached opposed conclusions regarding the addition of Cu on NiTi alloys¹⁸⁰⁻¹⁸². Discussion on this issue will continue after the scanning electronic microscopic findings are analyzed together with the atomic force microscopy and the nickel leaching.

TMA showed high resistance to the anodic polarization as the photographs show (photo 31). Based only on the photographic findings it can only be said that the specimens changed in color. This was the only change that could be seen at the surface. This is due to the fact that the metal undergoes an anodization that does not affect it structurally as much as other metals are. When referring to stainless steels, anodization is a well known method for coloring them. In fact, the relationship established between potential differences and colors obtained it is well known at the industrial field.

Photographs analyzed comprise different as-received archwires and archwires that were polarized. The archwires that were submerged for 30 days in the HBSS did not show macroscopic differences when compared to the as-received group and photographs are not shown although other techniques have been used to assess any kind of change as it is seen at the SEM and AFM analysis.

4.4 Scanning Electronic Microscopy results

Scanning Electronic Microscopy is a widely used method in corrosion studies. It is performed in order to assess the effects that corrosion has on the surface of specimens. In order to discuss results, three groups will be established according to the materials: stainless steel, NiTi and CuNiTi and finally TMA.

Scanning Electronic Microscope images that will be used for discussion purposes are as follows:

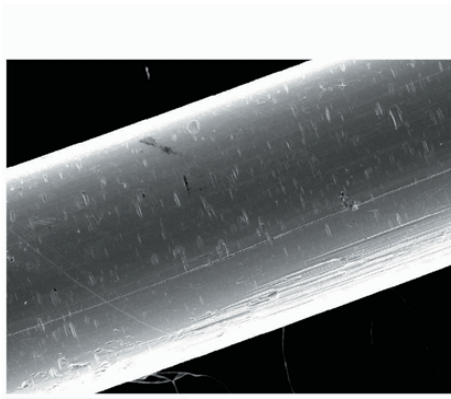


Photo 88

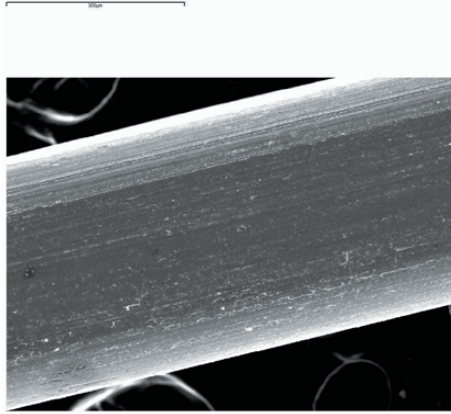


Photo 89

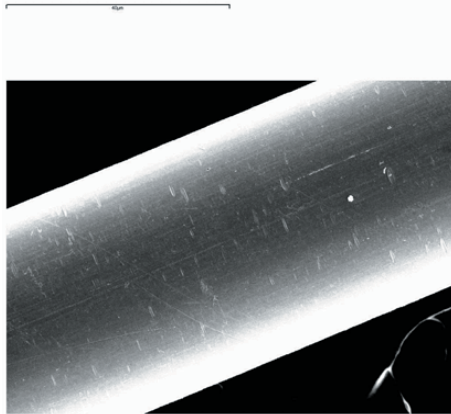


Photo 98

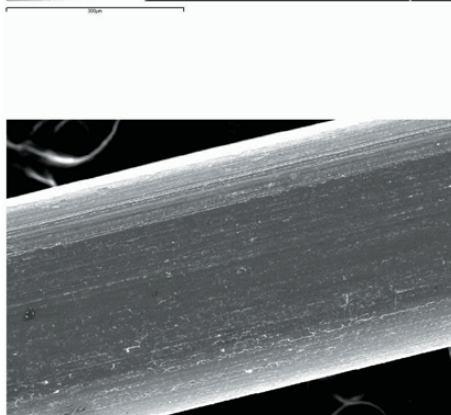


Photo 99

Photo 90

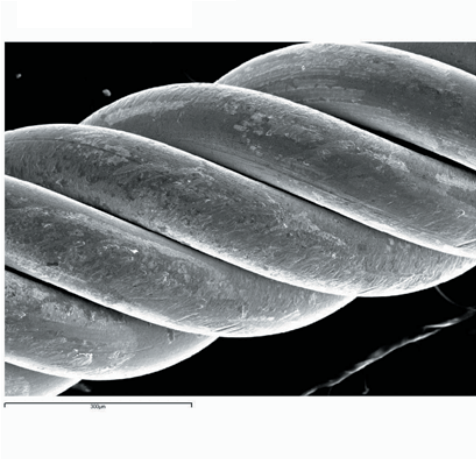


Photo 91

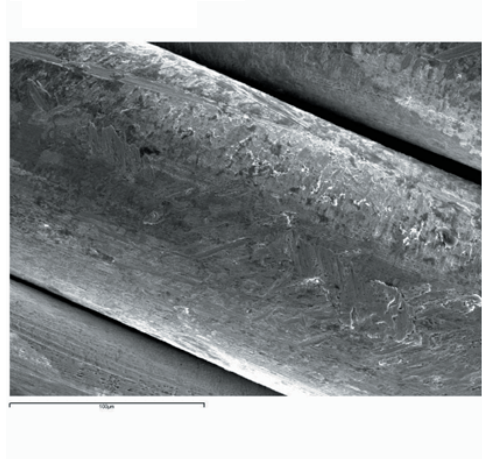


Photo 92

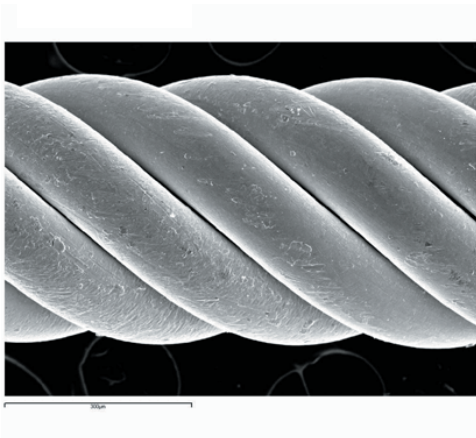


Photo 93

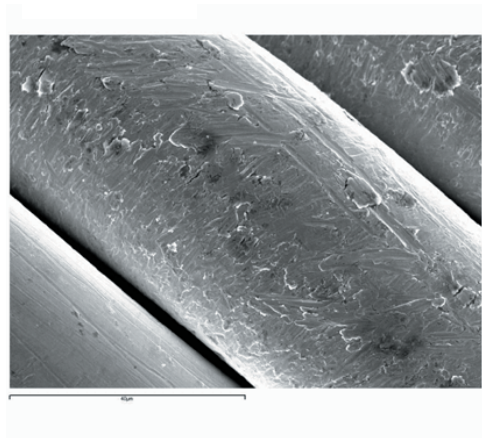


Photo 94

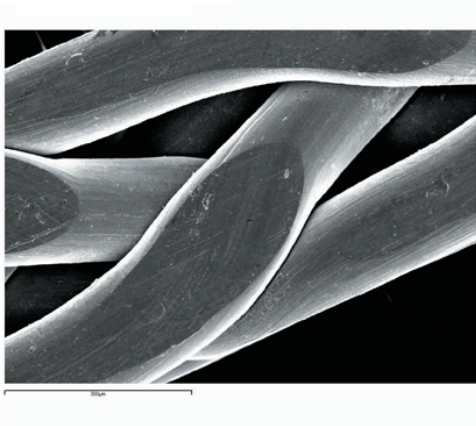


Photo 95

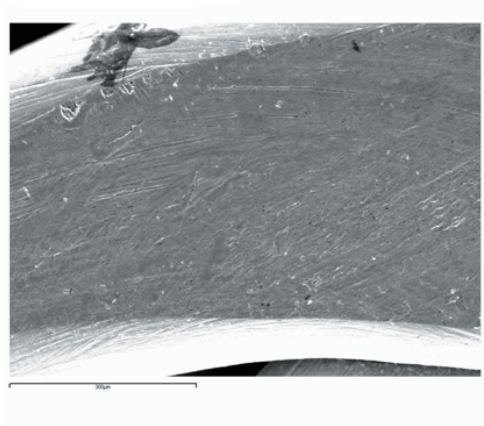


Photo 96

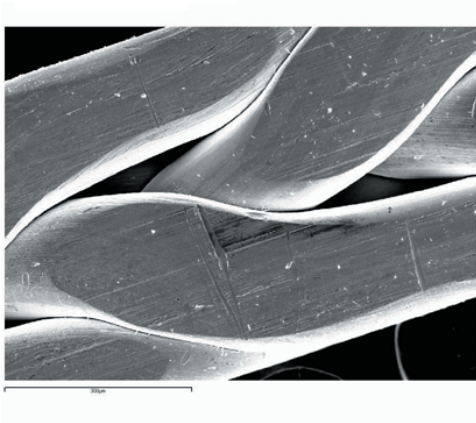


Photo 97

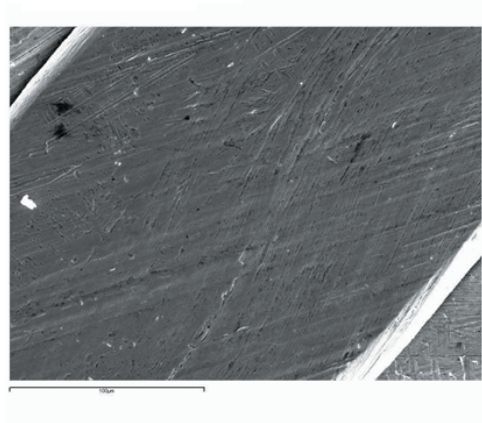


Photo 100

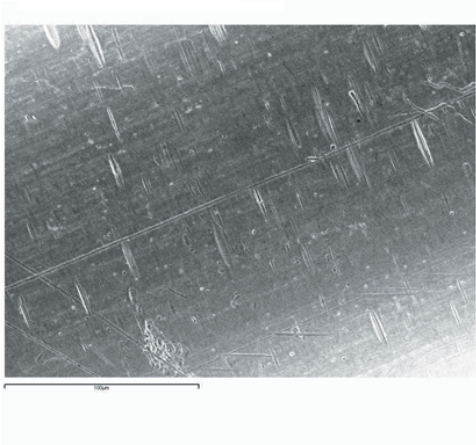


Photo 101

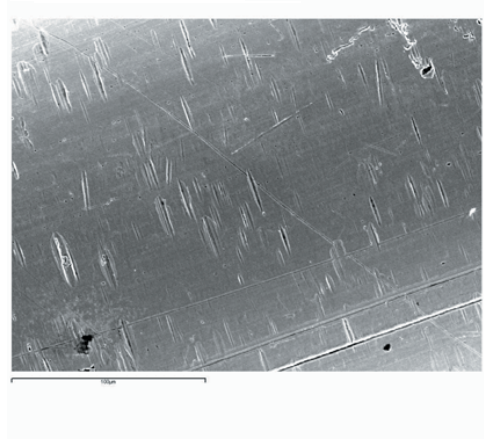


Photo 102

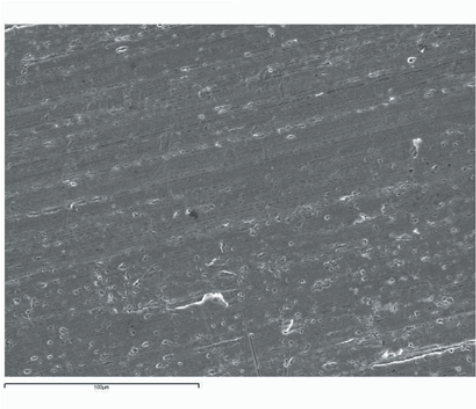


Photo 103

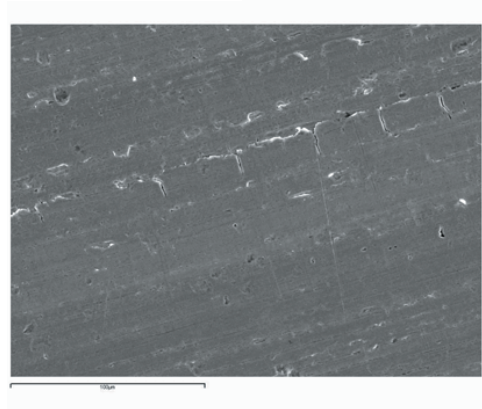


Photo 104

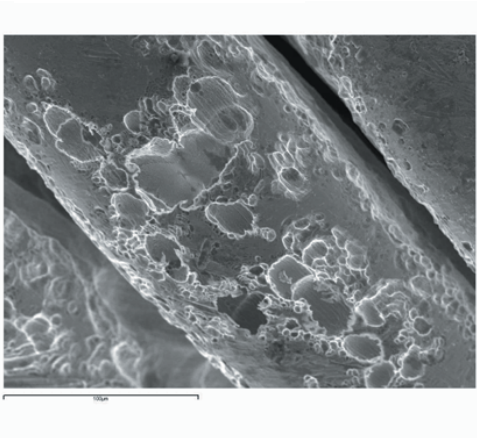


Photo 105

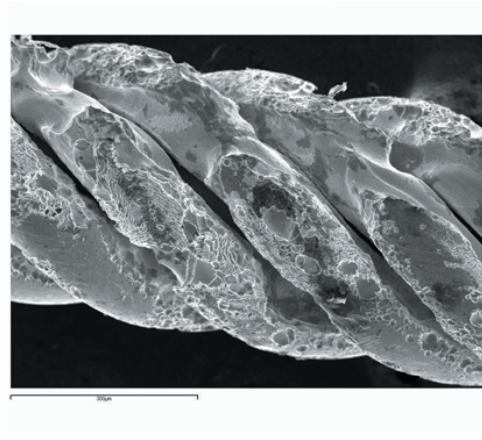


Photo 106

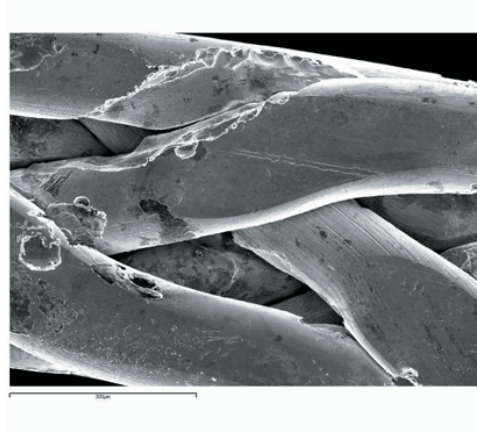


Photo 107

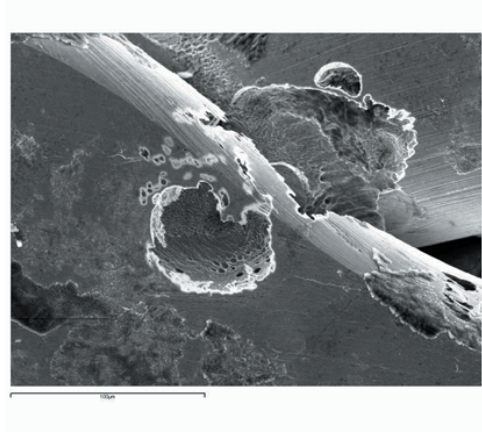


Photo 108

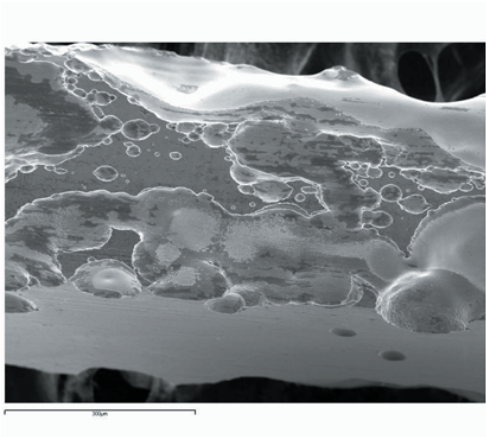


Photo 109

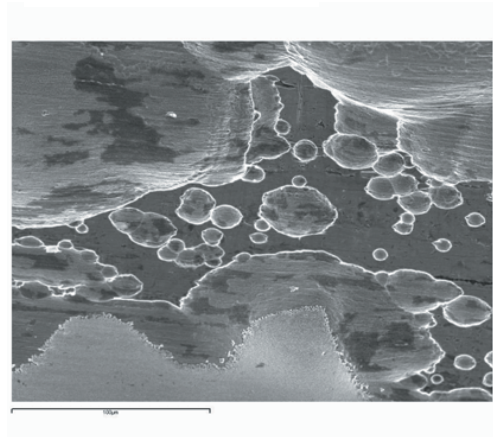


Photo 110

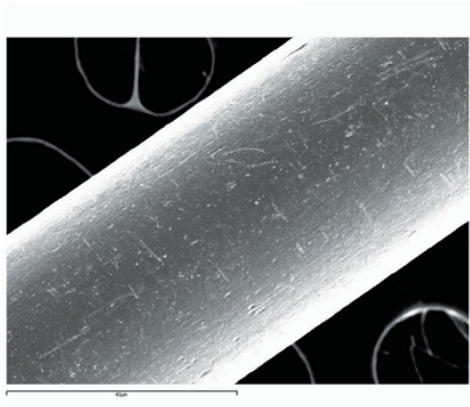


Photo 111

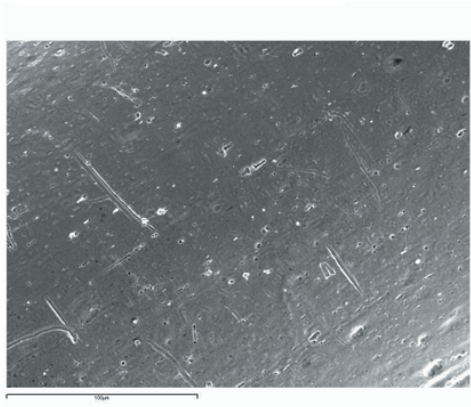


Photo 112

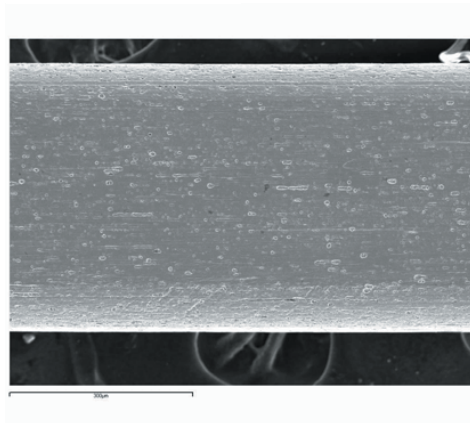


Photo 113

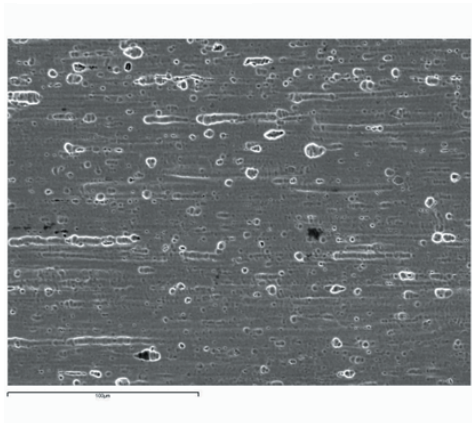


Photo 114

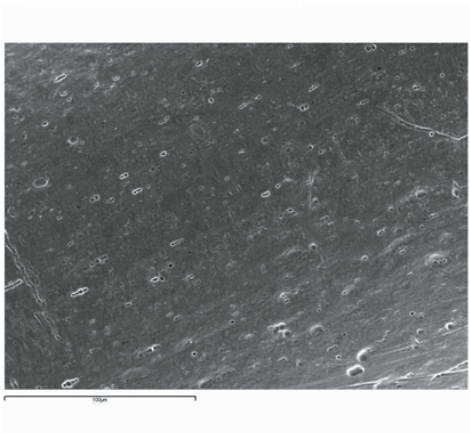


Photo 115

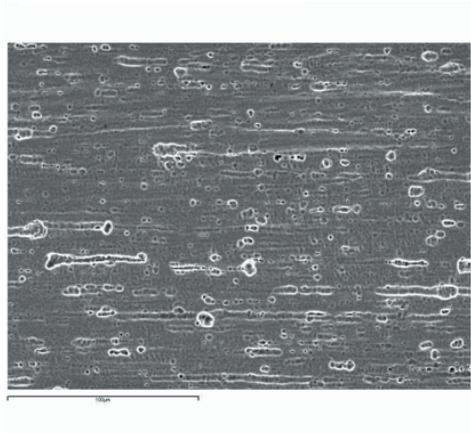


Photo 116

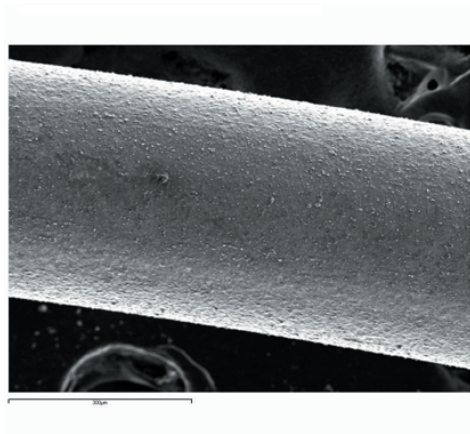


Photo 117

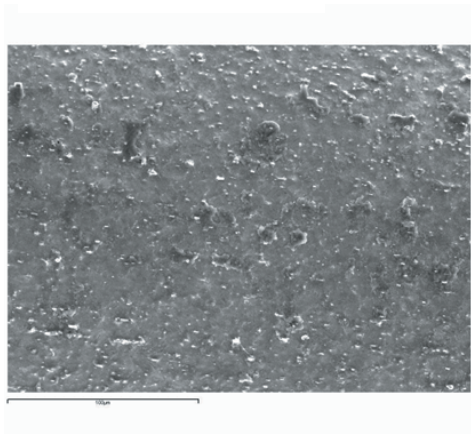


Photo 118

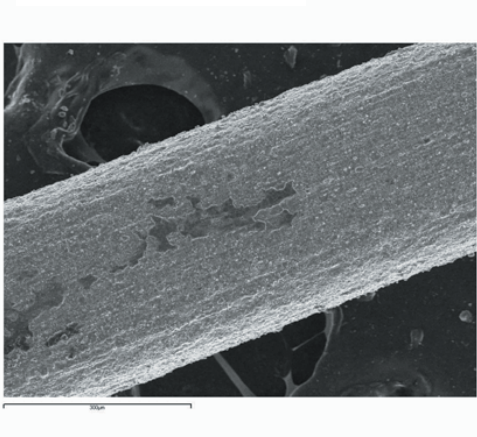


Photo 119

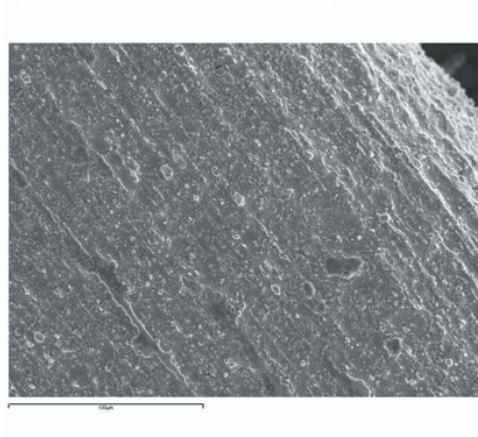


Photo 120

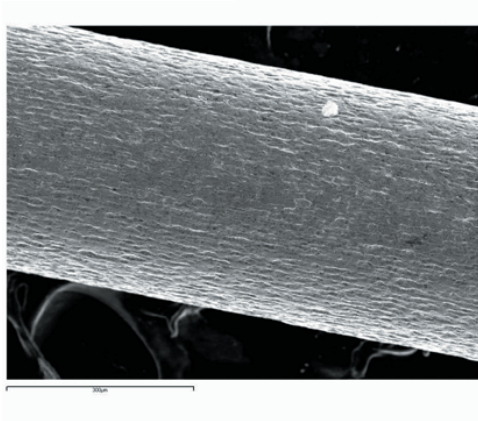
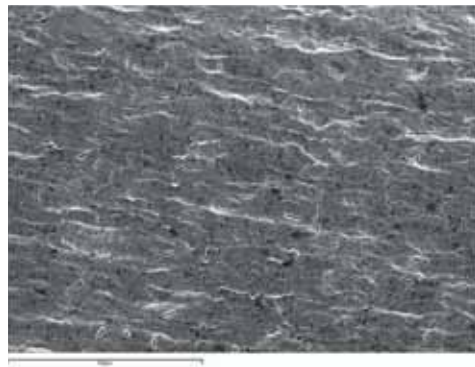


Photo 121



Respond wires show a rough surface due to the manufacturing procedure (photo 32). The as-received scans show surface defects that mainly follow three different orientations: longitudinal to the single wire that conforms the strand, circular defects following the perimeter of the single wire and oblique to the previous mentioned defects. These surface defects are due to the manufacturing process that leads to the braided wire. The higher the number of industrial steps required to manufacture a wire the higher the number of defects that can be added up in terms of lack of homogeneity at the surface. Besides of the standard wire manufacturing procedures, the Respond wire needs a twisting process in order to obtain the braided wire. Besides a rough surface finish, small black pores can be seen on the surface that imply a lack of metal that will eventually, together with the grooves resulting from the manufacturing process, become points where corrosion will start.

D-Rect as-received scans show what it was just stated above regarding the steps of the manufacturing process (photo 35). Given that this wire requires a final manufacturing step in order to flatten it so to obtain a squared section, defects of the flattening process can be clearly seen at the scans. Pores can also be seen in a bigger quantity than the present at the Respond wire. The flattening process also gives rise to irregular edges as it can be seen at the images. Therefore, the standard defects of manufacturing due to wire drawing or pickling are present and two new kinds of defects due to the particular manufacturing of this wire will also be a corrosion starting point: the deep grooves and the irregular edges resulting from the squared configuration of the wire. Besides that, it can be seen that there is a high porosity on the surface of the wire.

The stainless steel 0.016 (photo 41) wire in the as-received state shows a highly damaged surface. Longitudinal defects can clearly be observed along the 160 scan that may be due to the drawing process (photo 88). Perpendicular to them there can be observed elongated defects that follow the circular surface that seem also to be due to the manufacturing process. A mild surface porosity of the wire can also be observed.

The as-received stainless steel 0.016x0.022 (photo 38) wire shows higher quality surface finish than the previous wires. Manufacturing defects are not as obvious but elongated surface pores and grooves due to a lack of metal can be seen at the 160 scan (photo 89)

The scan images taken at the immersed wires clearly show differences at the surface of the wires (photo 42 and 39 respectively).

Immersed Respond 160 and 500 (photos 90 and 91 respectively) scans show a rougher surface when compared to the as-received state (photos 92 and 93 respectively). Porosity seems to have

increased as seen at these scans and also confirmed by the 1500 scans presented at the results chapter.

D-Rect 160 and 500 scans comparing the immersed state (photos 94 and 95 respectively) and the as-received wires (photos 96 and 97) respectively do not seem to show clear differences among both groups but 1500 augmented scans presented at the results chapter show an increase in the pores size becoming more elongated and losing their initial round defined shape.

Stainless steel 0.016 scans taken at 160 showing the as-received state (photo 88) and the immersed condition (photo 98) do not show significant differences. A close look at the 500 scan of the immersed specimen (photo 100) shows that the pores are a bit bigger and they are characterized by the presence of a white perimeter that although they can also be seen at the as-received state (photo 101), that are not that common. It seems to be a higher density of pores at the immersed scan. The 1500 augmented view shown at the results chapter confirms the stated findings. Pores seem to become bigger and more elongated after the immersion test and there can be seen the new white perimeter around most of the biggest defects. Small pores can also be seen.

Finally, the stainless steel 0.016x0.022 wire shows slight differences between the as-received and immersed 160 scans (photos 89 and 99 respectively). At this view the immersed wire surface seems to a bit rougher than the one of the as-received specimen but this fact might be a bit difficult to objectively be stated. Comparing the scans taken at 500 augments differences can clearly be seen between both specimens. A higher density of pores can be seen at the immersed wire (photo 102) when compared to the as-received specimen (photo 103) together with an increased number of defects which are surrounded by a white perimeter. This can also be observed at the 1500 augmented views presented at the results chapter. Surface defects due to manufacturing processes can be also clearly observed at the 1500 magnified views.

All stainless steel wires studied presented manufacturing defects at the surface. These defects seem to be due to the drawing processes that are followed in order to manufacture the wires. As Hunt et al²² state, these defects may be the result of the wires being drawn through diamond dies during production with the resulting longitudinal grooving. Depending on the performed operation in order to obtain a given wire (braided wires) or a particular section (round or square) manufacturing processes are added. It seems that, according to the observation of the wires, the higher the number of mechanical processes are involved at the manufacturing of the wire, the higher the number of manufacturing defects are.

Immersion of the stainless steel wires in the HBSS for 30 days under a constant temperature of 37°C seems to introduce changes at the surface of the wires although they might not be considered really important. An increase at the density of surface pores and the white perimeter appearance at the pores is the most remarkable finding that can be seen when comparing the surface changes at both groups under scanning electronic microscope study.

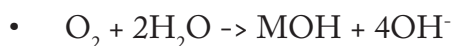
This initial corrosion stage could be explained by the pitting corrosion theory.

This kind of corrosion is the result of the local breakdown of the passive layer and subsequent contact of the underlying steel with oxygen. It mainly occurs in chloride, bromide or halide solutions. The chloride contained at the HBSS electrolyte could be acting as the corrosive element. A discontinuity in the passive film or a surface structural defect can act as the trigger. The underlying steel is dissolved leading to a concentration of positively charged metal ions. This causes negative charges, like chloride ions if it was the case, to move near the defect. Even if a neutral solution is used, a local pH drop to 2 or 3 could be observed, rendering the passive layer regeneration impossible.

The anodic dissolution of the steel leads to introduction of positive metal ions (M^+) in solution, which causes migration of Cl^- ions. Consequently, metal chloride reacts with water causing the decrease of the pH



The cathodic reaction given on the surface close to the pit follows:



Although pitting propagation phenomenon is well understood, pit initiation mechanism is not fully understood. According to Ryan et al¹⁸³, initiation has long been associated with MnS inclusions which are difficult to avoid in the steel-making process. It seems that the inclusions are surrounded by a Cr depleted region which is believed to cause the initiation.

According to Sourmail and Bhadeshia¹⁸⁴, when the passive layer is considered, the current density that can be measured at the surface is really small, of the order of $nA\ cm^{-2}$. But when a pit is produced, the current is found to exceed $1A\ cm^{-2}$. This is so because the pit, being the anodic point has a really small area when compared to the cathodic area, the unpitted steel. Then, for a given corrosion current if present it is greatly amplified at the pit. In the same way, chloride ions concentration around the pit can be thousands of times above the concentration of the solution considered as a whole.

Increasing the Cr quantity, or adding Mo or N enhances the pitting resistance.

The Cr-Fe-Ni matrix increases its localized pitting corrosion tendency and increases its resistance to crevice corrosion (especially referring to ferritic stainless steels) when Molybdenum is added. It is been empirically proven that Molybdenum content improves the resistance to corrosion of stainless steels to chlorides when used in coastal applications.

Localised corrosion (pitting and crevice) in acid-chloride solutions is also increased by nitrogen. Chromium and manganese increase nitrogen solubility while nickel acts in an opposite way in austenite steels. Excessive concentrations of nitrogen can precipitate in form of chromium nitrides. There are two equations that establish the contribution of each solute in weight to the pitting tendency of a material. They are as follows:

Pitting index for duplex stainless steels = $Cr + 3.3Mo + 16N$

Pitting index for austenitic stainless steels = $Cr + 3.3Mo + 30N$

Scanning Electronic Microscope images taken after potentiostatic anodic polarization was performed show clear effects of corrosion. Big corrosion pits can be seen in all stainless steel wires of the group.

The Respond wire shows a generalized affected surface after polarization. All the wires that form the strand have been severely damaged and unpitted stainless steel is not present. The 500 scan (photo 104) shows the typical pits that can be observed through all the exposed sides of the wire. When two pits unite their edges a massive lack of surface is produced as it can be seen at the 160 scan (photo 105).

The 160 scan taken at the D-Rect wire shows that this wire withstands polarization better than the Respond wire (photo 106). Unpitted stainless steel can be observed and pits seem to be mainly located at the edges of the wires that form this braided wire. The 500 scan allows the observation of a big pit that almost reaches one of the edges and small pitting defects that would eventually lead to the increase in size of the observed defect (photo 107). The scan allows the observation of unpitted stainless steel an oxide surface together with a bare metal surface.

The 0.016 and 0.016x0.022 stainless steel wires seem to behave in a very similar way to polarization. The 160 and 500 scans of both specimens (photos 108 and 109 respectively) show similar surface corrosive characteristics with reduced unpitted surfaces and different sizes of pitting defects. It is noteworthy saying that the edge of the 0.016x0.022 has been dramatically

affected. Edie et al²⁵ observed a similar finding. They noticed that pits occurred along the sharp edges of rectangular wires where the electric field would be the greatest.

NiTi and CuNiTi archwires seem to behave differently to the stainless steel archwires in both tests: the immersion test on HBSS and the potentiostatic anodic polarization test.

Initial 160 and 500 magnified scans of the as-received wires show that both wires have a rough surface finish but it is very different when compared to the stainless steel group (photos 110 and 111 for NiTi and 112 and 113 for CuNiTi at the stated augments). Surfaces do not present generalized grooving due to manufacturing processes as were observed at the stainless steels. The NiTi 500 scan shows discrete grooving perpendicular to the longitudinal axis of the wire that recalls the surface defects observed at the 0.016 stainless steel wires. Pickling of the surface is higher than the observed at the 0.016 stainless steel. The NiTi surface seems to have a high density of pores and some white points that are highly oxidized points but they are very scattered. According to Walker et al⁷ the bright white spots appear to be inclusions in the wire.

The low augmented NiTi scans are very similar to those obtained by other authors ^{7,9,12} with no significant differences to be remarked.

The immersed wire shows very small differences when the scans are compared to the as-received state. Being the NiTi an alloy resistant to corrosion, immersion on HBSS was not expected to induce surface changes on the wire. The 160 scan shows no significant differences but at the 500 scan a slight difference can be seen. When both scans are compared, NiTi (photo 114) and CuNiTi (photo 115), it can be seen that after immersion the pores seem to be dividing themselves in order to obtain a bigger pore, most times leading to an elongated pore. This is just a subjective appreciation of the scan taken and might not be a generalized process. The initially found bright white spots are not present at the immersed wire.

When potentiostatic anodic polarization is performed changes at the surface of the NiTi wire can easily be seen. The 160 scan of the polarized specimen (photo 116) shows a regularly spotted roughened surface. The 500 scan shows that porosity has completely disappeared (photo 117). An oxide layer is covering the whole surface. A big quantity of bright white spots appeared. The scan obtained is very similar to that obtained by Walker et al⁷. Elongated pitted defects are not seen as the scans Walker et al⁷ obtained after immersion on a fluoride environment but the increase in the number of white spots is in accordance with their findings.

Walker et al⁷ claim them to be inclusions at the wire. It can be said that they are highly oxidized spots that may coincide with a different element inclusion that undergoes a different corrosion pattern than the rest of the bulk alloy.

CuNiTi scan at 160 augments already shows the characteristic surface topography that this wire presents (photo 118). As already found by Fischer-Brandies et al¹³⁸ and Walker et al⁷ the observations that could be done about the surface topography of the wire are that it presents a rough surface, rougher than the NiTi wire, it shows longitudinal grooves and the characteristic surface of this wire seems to be due to the re-crystallized fine grains oriented in the direction of pull of the manufacturing process. Besides that, Fischer-Brandies et al¹³⁸ characterized some inclusions in the wire as Ti-rich inclusions of 2 μm long, C-rich precipitations and some surface defects at the edges of this squared wire. The scan obtained by the authors is almost identical to the obtained at the present research. Given that the scans obtained after immersion were not significantly different from the non-immersed wires it has been decided to show two 1500 augmented scans of a non-immersed and an immersed CuNiTi wire. Not really big differences appear to be found. As a subjective observation it might be said that the immersed wire shows an increased porosity but this might not be due to the immersion test but to the selected area chosen for the scan so it can not be attributed to the immersion.

Potentiostatic anodic polarization of the CuNiTi wire introduces dramatic changes at the surface topography. The characteristic topography previously described disappears and a very rough surface is presented. The 160 scan shows generalized roughening of the surface with an oxide layer present at the side shown at the scan. The edges of this squared wire can be seen to be really affected. The 500 scan shows the same findings (photo 119).

Immersion scans were not taken for the TMA wire because the immersion test was only performed for the wires susceptible of Ni release, and TMA does not contain Ni in its alloying metals. Given its high resistance to corrosion it is not expected that the surface topography of this alloy experiences significant changes at this immersion test.

TMA scans taken after polarization show a very rough surface, the roughest compared to the NiTi and CuNiTi wires. The 160 scan (photo 120) shows a regularly roughened surface that follows the longitudinal axis of the wire and the 500 scan (photo 121) shows the bright white spots that could be highly oxidized points of metal present at the alloy as inclusions. Patches due to corrosion products can be seen on the surface.

Although becoming very rough after potentiostatic anodic polarization, the NiTi, CuNiTi and TMA wires did not alter their general shape, keeping their section after the corrosion tests and so being more resistant than the stainless steel wires studied.

It could be concluded that the wires that are more resistant to potentiostatic anodic polarization in terms of maintaining the original surface topography are the TMA wires followed by the NiTi wires and finally the CuNiTi wires. All of them increase noticeably their surface roughness as the SEM scans show but their general shape and section are conserved. Immersion on the HBSS does not seem to inflict significant changes on the surface topography although small changes regarding porosity can be observed that might not be related to the immersion test but to the chosen region for the scanning and so this would require further research.

The stainless steel group of archwires shows low resistance to potentiostatic anodic polarization as the scans show. Pitting corrosion is severe after polarization and mild at the immersion test.

4.5 Atomic Force Microscopy results

As it has been seen, SEM scans are not clear when it comes to establishing the evidence of surface changes between archwires immersed for one month in HBSS compared to as-received archwires surfaces. In any case, conclusions drawn from the comparative study of the images obtained at the SEM are subjective in the sense that they rely on the qualitative aspects of the observed changes.

The reason for using the AFM technique is, as it has been said before, establishing whether the archwires immersed for one month in HBSS do really present surface changes that can be quantitatively measured when compared to as-received archwires surfaces.

One of the main points that had to be taken into account is the fact that archwires, as previously shown, present manufacturing defects in most of the archwires surfaces, no matter the alloy of the archwire. This could be a major problem when trying to answer the question: does HBSS affect the surface of the archwires when they are in contact with the solution for a month's time? In case that manufacturing defects are not detected nor taken into account, they could be responsible of the subjective evaluation of the changes in a particular sample without being related to the HBSS action on the surface of the archwires. That would be the case of two samples of the same alloy, one of which was initially more damaged due to the manufacturing procedures. In case that the most damaged sample was the one that had been used for the immersion test, it could erroneously be concluded that the observed changes at the surface are due to the HBSS action. So this fact

could lead to biased conclusions.

Manufacturing defects are sometimes clearly seen at the AFM scans. In order to obtain correct RMS manufacturing biased free sample measurements, these areas were avoided for RMS sampling. Segments of the same archwire were used for comparison purposes and hence reducing inter arch variability: a segment was used as the as-received control group and the other segment was tested at the immersion for one month for Nickel release analysis and AFM surface analysis.

It was decided to take ten random measurements of RMS values of both segments in order to compare them with a t-test. The areas used for the measurements can be seen at the results images (AFM photos 52-87) as green boxes.

RMS values allow a quantitative evaluation of qualitative changes induced at the surface due to the effect of the contact of the archwires with HBSS.

The measurements were done measuring RMS in μm so to be able to compare results with previous studies^{14,137}. In order to avoid manufacturing defects but at the same time being able to do a thorough sampling of the surface, a study area of $2\ \mu\text{m} \times 2\ \mu\text{m}$ was selected. Bigger areas would not allow such a big sampling and would easily include manufacturing defects that may include RMS values that are under the effect of increased roughness due to manufacturing defects.

Given the nature of the variable, reducing the study area to lower values would equalize roughness measures given that each RMS analysis is performed by using the number of events in the heights of the analyzed area. This would lead to misleading comparisons. It has to be recalled that AFM allows scanning areas from the atomic level up to hundreds of μm^2 so, zooming in the analyzed areas for a roughness study comparison could decrease the difference in roughness among specimens or, in any case, obtain misleading conclusions about the change in surface roughness.

AFM analysis led to see that the value is normally distributed when RMS is analysed. The software used allows to study the distribution that the value has, and it was seen that it follows a normalized distribution so a t-test for the significance of the difference between the means of the samples could be performed to see whether the change in RMS values after the immersion test could be said to be due to the effect of the solution. As it was said before, segments of the same archwire were used when comparing as-received and immersed RMS values. The samples were independent, that is, it was not the same segment the one under consideration but different

segments of the same archwire.

The null hypothesis is that the archwires do not present changes after being immersed for one month in HBSS when they are compared with a control group of as-received archwires. Therefore, any difference that could be found among the means of the RMS measurements of the two samples should not differ from zero in a significant way.

The statistical test chosen for the present research is the t-student test, which is thoroughly used in these kinds of studies.

The hypothesis was set in a directional way, that is, as changes in RMS are expected to be observed due to the immersion in the solution, a directional test is performed instead of the two-tail test that belongs to a non-directional set up.

All tobs but the obtained for the NiTi alloy show values higher than t value for a 0,01 level of significance in a directional test.

As a result of the obtained values it can be concluded that the likelihood of obtaining the values due to mere random variability, pure coincidence or a sampling error is as low as 1%. Therefore, there is a confidence of 99% that the observed values reflect something that is unlikely to be due to random variability. This would therefore be due to a genuine difference induced by the effect of the HBSS on the surface of the wires for the one month immersion test.

In the case of NiTi, no significant differences between the RMS means were found between the control group and the HBSS tested archwires. Then, it seems that this alloy remained unaffected by the contact with HBSS.

Widu et al¹⁴ also found no significant changes in the RMS values for some of the NiTi archwires they tested under corrosive environment. On the contrary, as they state, a smoothing of the surface was seen and they hypothesized that this could be as a result of a flattening of the peaks and troughs that resulted from production on the surface.

This hypothesis should be thoroughly tested using the very same sample and studying the effect of the corrosive media. As it was previously said, some samples could be more damaged than others and this could act as a bias factor when roughness is measured. Therefore, unless previously known damaged samples are used as both initial and test sample for RMS, measurements and changes have to be cautiously interpreted, especially when relatively large areas are examined as it

was the case of Widu et al¹⁴. Their AFM study areas were 100 μm x 100 μm , and the present study areas of 2 μm x 2 μm were selected from imaging at 20 μm x 20 μm .

As it can be seen at the photos 67, 70 and 79 of the AFM results at the 20 μm x 20 μm imaging of the samples, evidence of manufacturing defects are present. Therefore, if smaller sections are not taken this defects could act a as a bias factor. Furthermore, if a statistical study is not performed by randomly selected areas as small as 2 μm x 2 μm it is quite risky to assert that changes are due to the corrosive environment rather to a lack of sample validation.

In the present research, it can be seen that, after a careful study design it seems that archwires under one month immersion on HBSS present significant changes as measured by the variation in their RMS, except the NiTi archwires.

Following a significant order of variation the archwires could be placed as follows:

SS 0.016x0.022 (t_{obs} 6,67)

Respond (t_{obs} 5,09)

SS 0.016 (t_{obs} 3,66)

CuNiTi (t_{obs} 3,63)

D-Rect (t_{obs} 2,70)

NiTi (t_{obs} 0,55)

3D AFM images taken for the NiTi archwire seem to show an increased number of peaks and troughs after the immersion. But this is just a subjective appreciation from the obtained images.

In order to evaluate whether the hypothesis of Widu et al¹⁴ holds for the present research regarding NiTi, a profilometric study has been done by using the AFM software. The two 20 μm x 20 μm samples have been analysed through the profile tool. At a first stage, two profiles were obtained by doing a cross on the image in a North to South and West to East fashion. When parallel profiles to the initially taken were done, given the irregular surface under study, results varied highly in such a way that they were not representative and therefore they could not be used for comparison purposes. It was decided to take two randomly done tracings on the surfaces under study which would shed a mean profile value for the sample. They are as photos 122 and 123 show with the respective profile.

As it can be seen, the as-received sample has a profile with higher and more variable peaks than the one month HBSS immersed sample. So the hypothesis by Widu et al¹⁴ would hold for this situation although this should be more thoroughly studied and analysed. It seems in this case that the flattening of the peaks may be due to the corrosive test but again, as it was previously said, the same sample should be used for statistical purposes. In the case of this type of profilometric analysis, manufacturing defects can not be avoided because in order to obtain a global tracing the whole surface has to be covered, therefore, the need of using the same sample is almost mandatory.

A study by Bourauel et al¹³⁷ established three categories for AFM roughness measurements. For comparison purposes, they established the following categories according to the RMS values:

Smooth surface: $RMS < 0,2 \mu m$

Medium rough surface: $RMS < 0,4 \mu m$

Rough surface: $RMS > 0,4 \mu m$

According to these categories, changes in surface roughness of the archwires used in the present research would be as follows when mean RMS values are compared for as-received and one month HBSS immersed archwires.

Respond as received: $0,019 \mu m$

Respond immersed: $0,027 \mu m$

D-Rect as received: $0,010 \mu m$

D-Rect immersed: $0,024 \mu m$

SS 0.016x0.022 as received: $0,004 \mu m$

SS 0.016x0.022 immersed: $0,012 \mu m$

SS 0.016 as received: $0,005 \mu m$

SS 0.016 immersed: $0,008 \mu m$

NiTi as received: $0,019 \mu m$

NiTi immersed: $0,020 \mu m$

CuNiTi as received: $0,021 \mu m$

CuNiTi immersed: $0,041 \mu m$

The surface roughness changes due to HBSS would lead the Respond wire to change from a smooth surface to a medium rough surface, D-Rect changes from smooth to slightly medium rough, SS 0.016x0.022 keeps its surface in very smooth RMS values, SS 0.016 also keeps very low RMS values well under the smooth region, NiTi RMS values fall under the smooth region and

Photo 122

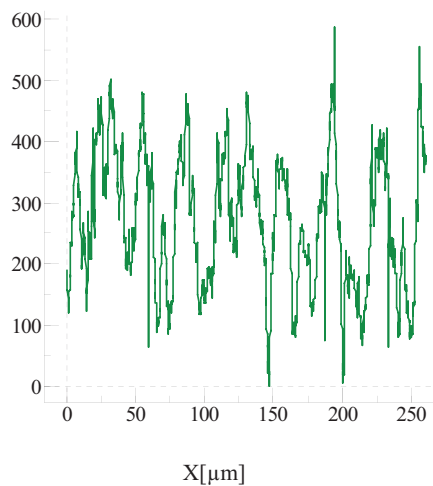
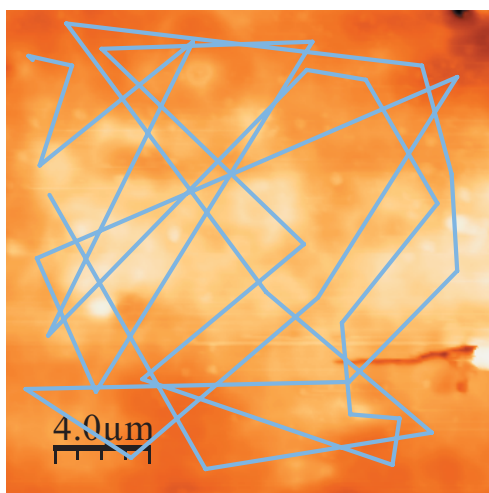
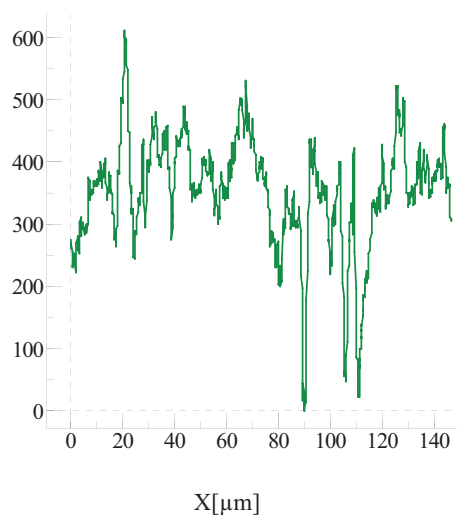
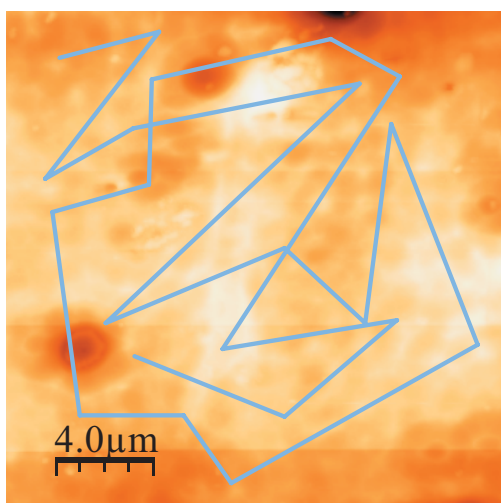


Photo 123



the biggest change is seen in the CuNiTi RMS change that shifts from almost smooth values to the rough RMS values.

Although RMS changes are obvious and significant, friction studies should be performed in order to see their clinical relevance. Studies on plaque adhesion could also be performed for the same purposes as a means of determining a clinical relevant change and not only a physical finding.

4.6 Nickel leaching results

A frame is needed in order to be able to grasp the magnitudes of Ni leached before starting to discuss the results obtained at the Ni release testing.

The European Union set a regulation limiting the Ni release of utensil and jewelry items at 0,5 $\mu\text{g}/\text{cm}^2$ of material surface during a week for at least two years¹⁸⁵. This would equal 0,071 $\mu\text{g}/\text{cm}^2$ on a daily basis.

For comparison purposes with the obtained data, ng and mm^2 will be used as units. So the above mentioned limits, once transformed to ng/mm^2 shed a result of 0,714 ng/mm^2 by day.

Another limit that could help as a frame of the obtained results is the limit that seems to impair the chemotaxis of leucocytes and stimulate neutrophils to become aspherical and move slowly. This limit was found to be 2.5 ng/ml (ppm) by Vreeburg et al⁶². Transformed to the units used in the results of the present research would be 2500 ng/l (ppb).

The previous data helps focusing on what could be considered dangerous limits for Ni detection. It should be kept in mind that Ni is commonly present in the daily diet. Oh et al³⁰ state that Ni present in daily average consumption of food ranges from 5 to 10 $\mu\text{g}/\text{l}$ and around 0,43 $\mu\text{g}/\text{l}$ in beverages. Other authors¹⁴⁰ give a daily range of 300 to 600 μg . A study performed in the United Kingdom established a dietary intake of 140-150 μg Ni from food and 100 μg Ni from cooking utensils¹⁸⁶. This data is in agreement with a study done by the New York State Department of Environmental Conservation¹⁸⁷ that found that the average person receives amounts of nickel in the order of 170 μg through ingestion and 0,4 μg through inhalation. Commonly assumed amounts of nickel by Nutrition Societies recommend a daily intake of 100 μg of Ni although it is considered that the real intake ranges from 160 to 900 μg Ni.

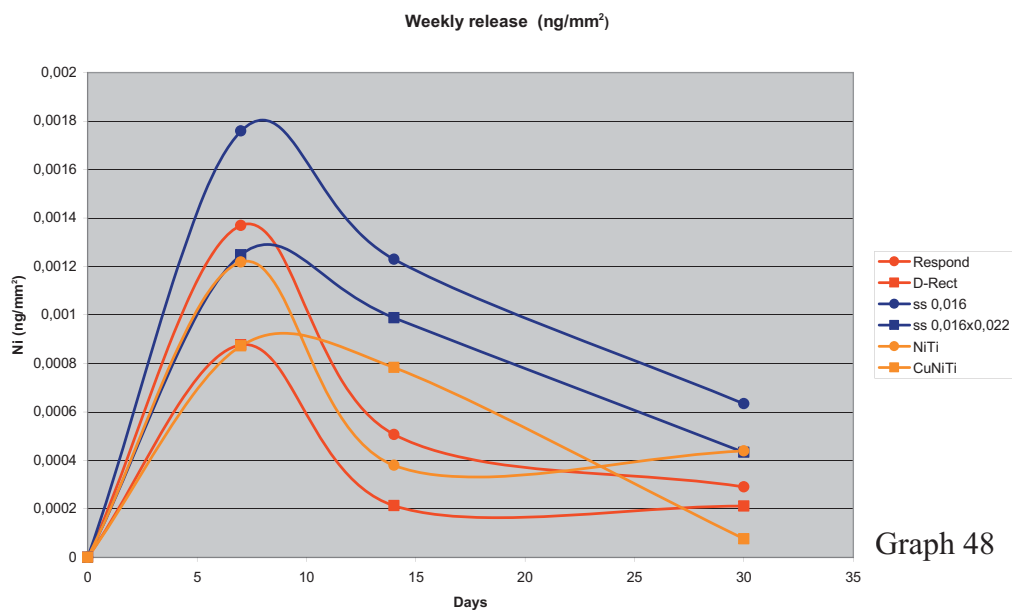
In any case, although legal regulations are the main frame for Ni release concerns and a daily intake has been observed to be around 160 to 900 μg Ni with additional Ni obtained from cooking utensils and air inhalation, the results obtained at the present research need being compared with in vitro release of Ni from orthodontic appliances. In vivo studies could also be used in order to establish comparisons and will be used for discussion purposes later on.

Some in vitro studies have been performed by different authors in order to establish the Ni release when exposed to artificial saliva preparations^{30,188-192} using the microscopic analysis of

corrosion and different sorts of chemical analysis. It has been seen that orthodontic appliances of different manufacturers, after being incubated in different artificial saliva preparations, release a quantity of Ni that range from 22 to 40 µg. The study performed by Park et al¹⁸⁸ was designed so that a full mouth orthodontic appliance model was exposed to a saline preparation. The Ni daily release was found to be around 40 µg. A study by Barrett et al¹⁹³ simulating the Ni release for a maxillary arch reached a maximum level of Ni leaching during the first week followed by a decrease in Ni release for the following three weeks.

These studies, although not covering the complete array of the existing scientific literature on Ni release are the most representative of the topic as shown by being frequently quoted in most publications. They can significantly form the frame of the discussion of the results that are now presented.

Basic initial results obtained by the Ni release analysis showed two basic graphs that will be used for discussion purposes.



Graph 48

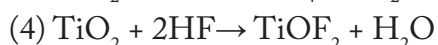
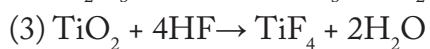
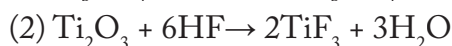
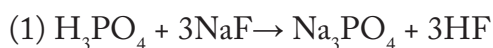
Graph 48 shows the trend in Ni release during the four weeks (weekly measurement

First thing to be noticed is that all archwires tested release Ni when in contact with the HBSS electrolyte. The highest amount of Ni is released during the first week for all archwires. There is a remarkable difference between the Ni amount released during the first week and the amount measured after two weeks of immersion. CuNiTi archwires keep a steady and mild decrease in

Ni release between the first and second week, which is followed by the ss 0.016x0.022 and to a lesser extent by the ss 0.016. Respond wires reduce their Ni release 2.7 times compared to the first week's measurement. The D-Rect and NiTi archwires undergo a Ni release reduction of 4.1 and 3.2 times compared to the measurement performed the first week.

When the Ni release measurement performed the second week is compared to the measurement done at the fourth week it can be seen that the Respond, the ss 0.016 and the ss 0.016x0.022 reduce the Ni released amount to a half of the value measured the second week. The D-Rect archwires keep the same Ni release trend without significant decrease. CuNiTi archwires experience an abrupt decrease: in two weeks there is a Ni release reduction of 11 times the amount measured the second week. NiTi archwires increased the Ni released value at the fourth week when compared to the second's week measurement.

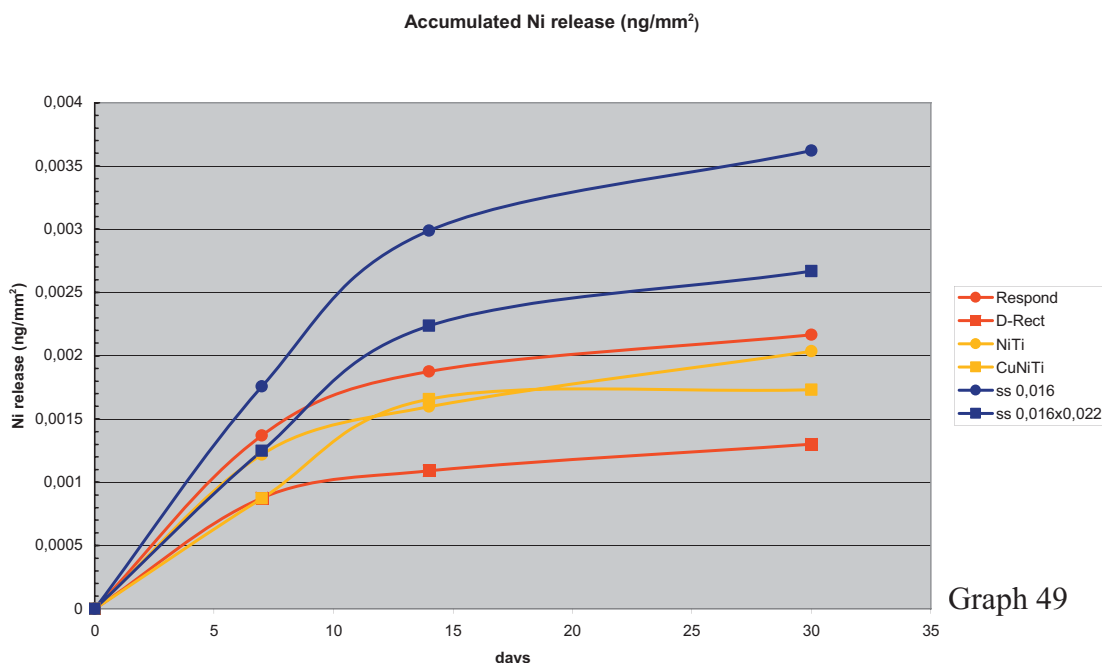
From the graph above it could be seen that the braided wires and the NiTi wires follow almost the same Ni releasing trend. The D-Rect and NiTi follow a specially similar trend when focusing on the Ni released between the second and fourth week. The stainless steel wires and the CuNiTi also show a similar trend but the CuNiTi archwires do not experience a big decrease of Ni release between the first and second week's measurements although they experience a dramatic decrease at the fourth's week measurement. CuNiTi's corrosive behaviour has been studied by some authors as being different from the rest of alloys. The Ni release behaviour found at the present research may have to do with the hypothesis that Walker et al⁷ hold. After studying different prophylactic agents, they found that even fluoride did not have a statistical effect on the tested mechanical properties of the CuNiTi wire. It was hypothesized that the apparent lack of fluoride effect might be related to the elemental composition of the CuNiTi alloy. They claimed that the addition of copper to NiTi alloy not only enhances the thermal reactive properties of the metal, but, according to Boyer et al¹⁹⁴, it acts as a relative inhibitor of reducing acids, such as HF. Therefore, Walker et al⁷ state that given that HF, reported to be generated in the presence of sodium fluoride (1), can then dissolve the titanium-based oxide layers as illustrated in equations presented in their study (2-4)



However, as Iijima et al¹⁷⁹ state, the decrease in inhibition characteristics of copper in the alloy and the reported increase in the concentration of the element at the alloy-oxide interface might

protect the wire from subsequent hydrogen penetration.

All wires with the exception of NiTi seem to decrease the ability of releasing Ni although being more time in contact with the HBSS electrolyte (two weeks) when comparing the amount leached after two weeks and the amount of Ni released between the second and fourth week. It should be kept in mind that each time a measurement is done, a complete extraction of the electrolyte is performed and the vial is again filled in with a new HBSS 4 ml. Then, NiTi wires seem to keep a good enough amount of Ni at the archwires surface that makes possible that in two weeks time of contact with the electrolyte is able to get an increased measurement of Ni leaching compared to the obtained for one week at the measurement taken at the second week. This should not be that surprising because the amount measured is obtained during two weeks. So the graph should not be mistaken or misinterpreted.



Graph 49

A cumulative trend would help us obtain a better understanding of the Ni release for the wires. This is the purpose of graph 49 presented also shown at the results chapter.

This graph shows an approximation to the total values of Ni released during a month of exposure to HBSS electrolyte in the study conditions. The highest amount of Ni released was performed by the ss 0.016 and ss 0.016x0.022 wires, followed by the Respond and NiTi wires which released almost the same amount. The CuNiTi and the D-Rect wire released the lowest amounts of Ni at the end of the test. Comparing the obtained results with the highest Ni released

value of the ss 0.016 archwire it can be seen that it is 1.35 times the amount released by the ss 0.016x0.022, it is 1.67 times the amount released by the Respond wire, it is 1.77 times the amount released by the NiTi, 2.09 times CuNiTi's release and 2.77 D-Rect's Ni leaching value.

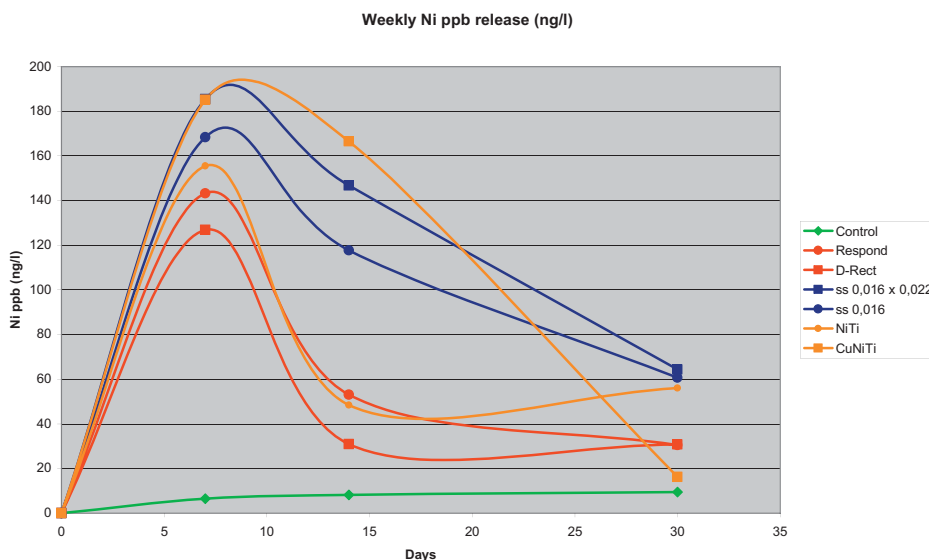
Summing up, the ss 0.016 wire releases in one month roughly one third more Ni than the ss 0.016x0.022 wire, double the amount of Ni than Respond, NiTi and CuNiTi wires and almost three times the amount that D-Rect wire releases.

The control vial shed insignificant Ni levels, so Ni measurements obtained are due to Ni released from archwires alone. The following table and graph show the directly obtained results without being adapted to the lengths, surfaces and number of arches embedded in each vial. They are presented with the only purpose that the Ni leached at the control vial can be seen to be insignificant.

Numerical data is shown in table 20 and graph 50 depicts the data.

Released Ni according to the archwire (ppb= ng/l)							
Days	Control	Respond	D-Rect	ss 0,016	ss 0,016 x 0,022	NiTi	CuNiTi
0	0	0	0	0	0	0	0
7	6,54	143,33	126,95	168,35	185,53	155,6	185,23
14	8,21	53,05	30,95	117,65	146,78	48,39	166,53
30	9,43	30,46	30,7	60,67	64,36	56	16,21

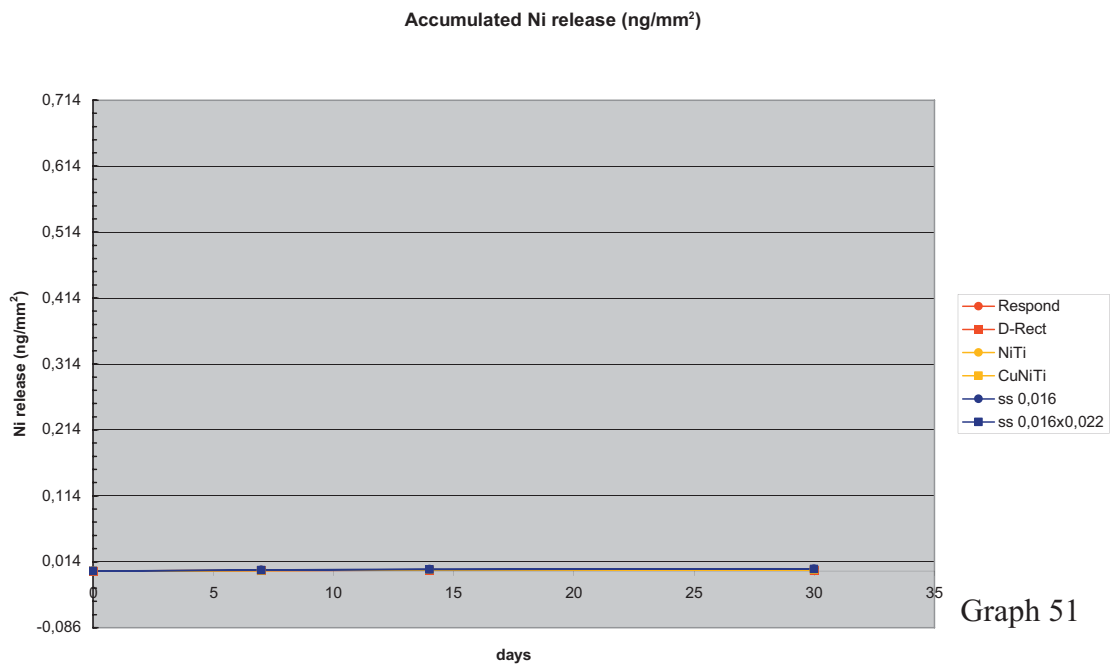
Table 20



Graph 50

The obtained results are in agreement with Barrett et al¹⁹³ findings. For Ni release they observed that it reached a maximum after approximately 1 week and then the rate decreased for the following 3 weeks in both stainless steel and NiTi wires.

The obtained results should now be framed taking the initially presented limits into account. It was seen that the limitation set by the European Union was 0,714 ng/mm² by day. If the accumulated graph was scaled to see how much Ni release the archwires present compared to the daily limitation it would look as shown in graph 51.



Graph 51

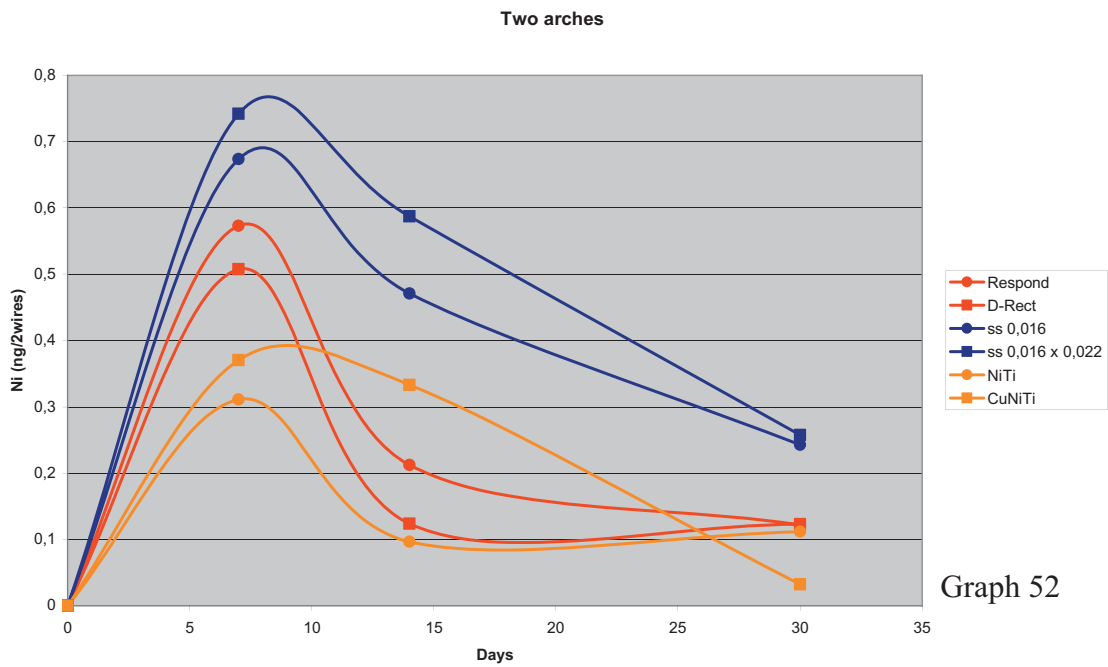
It can be seen from the graph that not even the total amount of Ni released by the archwires for a month reaches the daily value at all. In fact the Ni released could be neglected.

If total Ni per arch released was used to set the same comparison, instead of using a calculation per mm², the 4 ml of extracted HBSS electrolyte would lead to the results gathered in table 21.

Ni released (ng/both wires)						
Days	Respond	D-Rect	ss 0,016	ss 0,016 x 0,022	NiTi	CuNiTi
0	0	0	0	0	0	0
7	0,57332	0,5078	0,6734	0,74212	0,3112	0,37046
14	0,2122	0,1238	0,4706	0,58712	0,09678	0,33306
30	0,12184	0,1228	0,24268	0,25744	0,112	0,03242

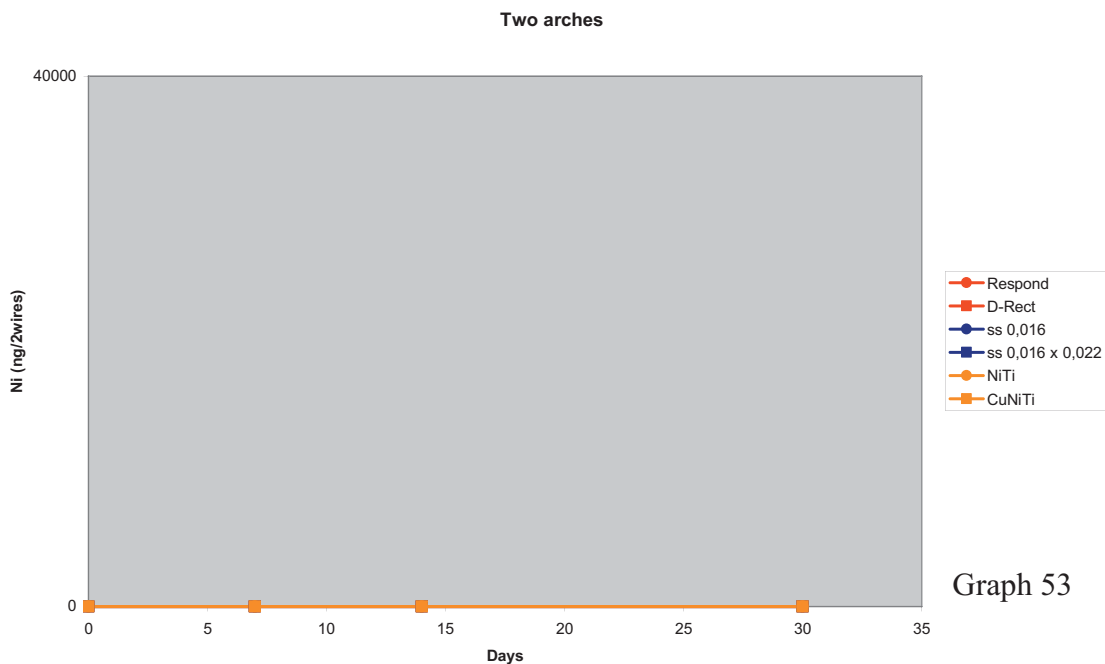
Table 21

The above results have been adapted for a full appliance (both arches). Graph 52 shows these results.



Graph 52

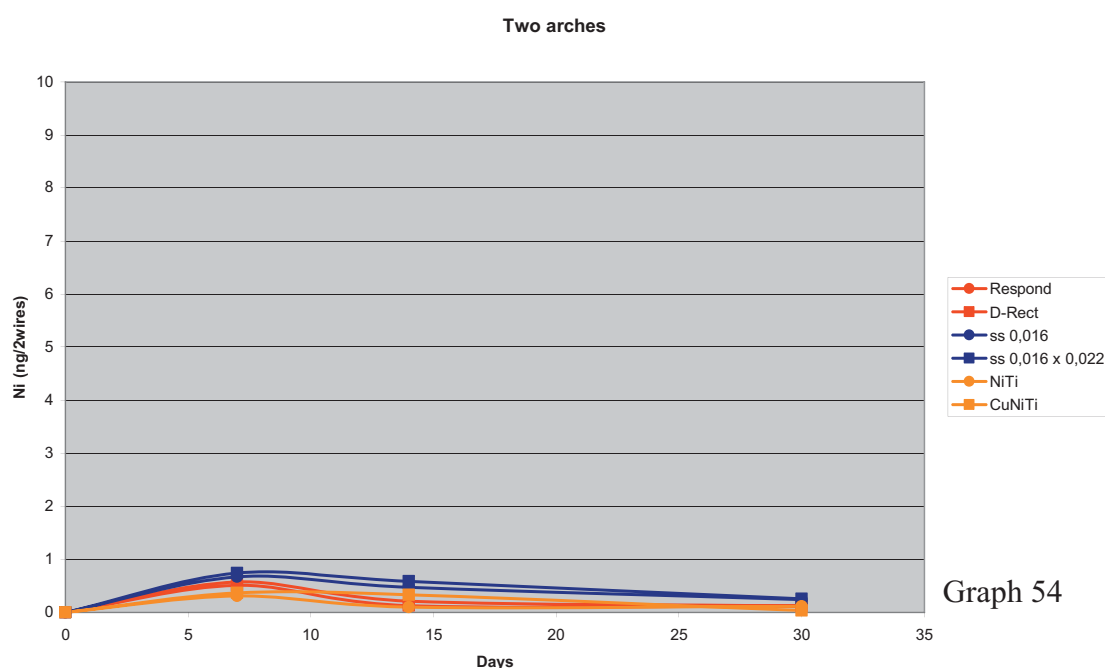
Previously cited studies found that archwires released a quantity of Ni that range from 22 to 40 μg for a two arch setting. That means that the range would be 22000 to 40000 ng. Although the above graph only depicts the Ni released in each vial for the equivalent of two arches (not by mm^2) it can be appreciated that the amount of Ni released would be insignificant. The above graph rescaled with the range of previous studies would be as depicted in graph 53.



Graph 53

Therefore, it can be seen that not even in a month, the previously quoted range is reached. Significance of the diet should always be accounted for.

A special limit that was also previously mentioned is the 2,5 ng/ml that was seen to alter leucocytes and neutrophiles. This would equal 10 ng for the present research given that the measurements have been performed on a 4 ml vial basis. Considering the above shown graph, even this limit is very much above the obtained Ni values. For comparison purposes the scaled graph that it is being referred to would look as shown in graph 54.



According to the actual knowledge, and comparing the obtained results to the most significant available studies of the scientific literature on the topic, the nickel release for the tested wires seems of very little concern as long as health is referred to.

With the Ni releasing accumulative trend shown in graph 49 some interesting predictions could be done.

In case the studied wires kept the same Ni release trend, how much time would it be needed to get to the maximum levels established as limits?

This calculation has been performed taking the slope of the curves of the accumulated values graph. An assumption has been made: the arch would keep the slope described by the second and third measurements of Ni release. Although this would not be a constant it could be said

that it is at least the maximum rate of Ni release that the arch would get compared to posterior measurements. So, the amount of time calculated would be an approximated result to a probably higher value.

The slope (m) of the lines was obtained by using the value for the 30th day (y_{30}) and the value for the 14th day (y_{14}) with the difference of 16 ($x_{30}-x_{14}$) days. The following are the expressions for the slopes

- Respond: $(0.021-0.018)/16$
- D-Rect: $(0.00130-0.00109)/16$
- SS 0.016x0.022: $(0.0026-0.0022)/16$
- SS 0.016: $(0.0036-0.00130)/16$
- NiTi: $(0.0020-0.0015)/16$
- CuNiTi: $(0.0017-0.0016)/16$

Then for each archwire, keeping the slope found for the Ni releasing trend of the archwire, x was obtained for the y set at 0,714 ng/mm² by using the commonly known mathematical equation:

$$y-y_1=m(x-x_1)$$

where m stands for the slope, and y is the set value for the limit at 0,714 ng/mm², and it was calculated in the following way:

$$0.714-y_{14}=\text{slope}(x-x_{14})$$

(see table 14 for values)

where the only unknown value is x for y limit at 0,714. The results obtained, once transformed in years are as follows:

- Respond: 107 years
- D-Rect: 147 years
- SS 0.016x0.022: 72 years
- SS 0.016: 49 years
- NiTi: 71 years
- CuNiTi: 409 years

In order to reach the maximum limit established of 0,714 ng/mm² for a daily amount the archwires would need the time shown above.

The reason of performing the calculation is not obtaining an exact prediction but getting the big picture of what the obtained results would imply for clinical concerns.

The Ni leaching test has some limitations. The test is an approximation to the amount of Ni that would be leached to the mouth by the arches. As it has been shown it is a non significant amount. This quantity of Ni should be added to the Ni leached by the brackets that hold the wires and the metallic ligatures that might be present.

In vitro conditions are very controlled conditions while the clinical scenario is not. The large amount of factors that come into play in every patient should be not forgotten. Saliva's pH, the use of fluoridated mouthwashes or products with chlorhexidine, the everyday contact with chloride (water of swimming pools) or with sea water could increase the rate on Ni release, but it is impossible to obtain an experimental model for predicting this phenomenon and get recommendations that would be useful for everybody, considering also the large array of appliances combinations that could be bonded in the mouth.

According to some studies, pH seems to be one of the most important factors related to Ni release. Both intrinsic pH saliva conditions of the patient and fluoride concentration have been found to be very closely linked to surface corrosion of titanium-based alloys^{195,196}. The acidic pH, may it be intrinsic in origin or fluoride influenced by toothpastes and mouthwashes, has been seen as an important factor in the breakdown of the passivating films leading to corrosion and hydrogen embrittlement of titanium-based alloys^{195,197}. Schiff et al¹⁰ found that some well known mouthwashes have an important influence on the corrosive behaviour of archwires and concluded their study by giving recommendations depending on the archwire ligated in the mouth in order to minimize corrosion and their consequences. A study by Huang et al¹⁵ performed on NiTi wires immersed on different pH solutions showed the dramatic influence that pH has on Ni release. For the Ormco archwires they tested, when a pH of 2.5 was set, the Ni released was roughly 20 times the amount released for the wires immersed on a 6.25 solution. Kaneko et al¹² are very clear with regards to their recommendations after their study. They said that orthodontists should avoid as much as possible placing wires with a titanium protective film in contact with prophylactic agents, toothpastes or dental rinses that contain fluoride.

Bending might act as a factor that increases Ni release. Archwires rarely remain passive in mouth. When engaged to the brackets they are most times trying to recover their original arch

form delivering a force that drives teeth movement. Under cyclic loading archwires may have a different Ni release patterns.

When dealing with the real environment where archwires act, it has to be kept in mind that the archwire acts as the anode and the saliva acts as the electrolyte, which is normally studied in combination with a great number of products in solution.

Determining the cathode is more difficult than establishing the anode and the electrolyte. In real conditions, archwires get in contact with metal brackets and most times also with metallic ligatures while the treatment progresses. Some studies have also dealt with this issue^{29,31}. Archwires follow a particular sequence and they are replaced with a given schedule. Different cross sections and materials are used during the same treatment. The complexity of the real scenario could even get more difficult to analyse if reconstructive materials used in general dentistry and prosthetic and surgical materials had to be taken into account (metallic crowns, amalgam fillings, composite reconstructions, implants, etc). This would obviously affect the anode in case that contact (direct or indirect) between both was present.

It should also be recalled that corrosion cells can be formed in a single structure (the archwire, for instance). In other words, areas acting as the cathode and anode could be present at the very same archwire. In the case of the archwires used in orthodontics, the presence of corrosion cells could be due to structural differences at the metal surfaces, a difference in phases of the metal, changes at the passivating film or even changes due to the manufacturing process in the same component.

All the above mentioned factors have not being taken into account in the experimental phase of the present thesis. They have been presented so to understand the complexity of reproducing the real scenario and the limitations of the present findings. This corrosion study only focuses on the archwires as independent units, so galvanic effects have not been studied.

With regards to the electrolyte, it should be kept in mind that variations could be found when comparing different points in an in vivo set-up. The electrolyte can be a limited volume that covers the metal, may it be adsorbed or condensed over it. In vivo situations present pH variations among different patients due to personal characteristics, diet differences and products used for hygienic dental treatment like chlorhexidine mouthwashes as said before. Adult patients can also present a considerable variability in saliva segregation due to physiological conditions or even medication.

So again the obtained results have to be put in the context of an in vitro experiment.

In order to simplify the calculations performed, the braided wires surfaces have been established as if they were round or square wires of that given diameter. Given the braided nature of the wire it is really difficult to calculate the exact exposed area of the wire, so that is why this has been simplified. In any case, the results of Ni leaching for the braided wires might not vary significantly if the exact surface was known. Anyhow, given the Ni release ranges obtained, this kind of discussion would be irrelevant.

An important finding of the Ni release test is the fact that stainless steel wires release more Ni than NiTi and CuNiTi wires although they do have a reduced Ni % in composition. Two kinds of considerations could be done.

First is that stainless steel wires should be kept in mind as wires that leach a higher amount of Ni that would in the end interact with the host.

Second, NiTi and CuNiTi wires would leach less Ni but the concern should be focused on the fact that they have an almost 50-50 proportion of Ni-Ti meaning that a large amount of Ni can be in direct contact with the different kinds of mucosa present at the mouth on a daily basis. So these wires do not leach a large amount of Ni and they have the ability of keeping it as a structural element which in the end can also be a drawback.

But again, these considerations are done on really small amounts of Ni leached.

The weights of some archwires were analysed so that together with the results of Ni leaching, the amount of Ni loss could be discussed. The weights results were as shown in table 22. Note that (u) stands for upper archwire and (l) for lower archwire.

	TMA	Drect	Respond	16x22	16	NiTi (u)	NiTi (l)	CoNiTi (u)	CoNiTi (l)
1	0,08778	0,2588	0,1253	0,28786	0,13776	0,08744	0,09856	0,12117	0,1143
2	0,10838	0,29072	0,12338	0,27486	0,13694	0,08612	0,09284	0,13312	0,10903
3	0,10762	0,24444	0,1257	0,28255	0,13792	0,10052	0,08623	0,1452	0,13498
4	0,085	0,23176	0,12818	0,25748		0,08233	0,07293	0,12332	0,12503
5	0,08603						0,0827	0,1476	
6	0,10766								
average	0,0970783	0,25643	0,12564	0,2756875	0,13754	0,0891025	0,086652	0,134082	0,120835
gr Ni	not present	0,0205144	0,0100512	0,022055	0,0110032	0,0490064	0,0476586	0,067041	0,0604175

Table 22

Weights variability is of little importance although they could affect Ni release obtained results.

If great structures were being studied this issue could alter the results and would of special concern when limiting amounts would be under consideration. But again, this is not the case.

Weights variability is a good parameter in order to study the care that manufacturers put in the manufacturing process. As it is seen, direct conclusions can be drawn if this variability is seen on archwires of the same length: there is a point at the manufacturing process where the composition is altered although the manufacturer might claim a particular % composition for the archwires.

4.7 Calorimetry results

The purpose of the Differential Scanning Calorimetry testing was to study the transformation behavior of the CuNiTi and NiTi wires and establish their phase transition temperatures for as-received wires and then compare them with the results obtained at the DSC testing in wires that were immersed for 30 days in the HBSS solution and wires that had undergone anodic potentiostatic polarization.

CuNiTi

Different authors have already dealt with DSC on NiTi and CuNiTi archwires^{138, 198-201}. Some of them also studied the single-temperature variant of CuNiTi that is the object of the present research. In the case of CuNiTi alloy, some studies deserve a particular attention given the relevance of their findings. One is Mallory's et al²⁰² study on the observation and explanation of "Dead wire" phenomenon for 35°C copper NiTi and a study by Biermann et al²⁰³.

Mallory et al²⁰² together with previous reports claimed to have observed a phenomenon by the name "dead wire" detected in some 35°C CuNiTi wires that had been engaged in the mouth during orthodontic treatments. They thought that a change in the phase transition temperatures had somehow occurred rendering the wire "useless" for the purposes for which it had been manufactured.

The transformation behavior of Ormco's 35°C Thermo active CuNiTi wires had been previously studied by Fischer-Brandies et al¹³⁸. They found that these wires had a normal martensitic-austenitic transformation, that is, R-phase transition was not present. They found that the wires

were fully martensitic at room temperature and developed the shape memory effect in a one-way fashion when heated above A_f . They were found to be fully austenitic at body temperature. The values obtained by the Fischer-Brandies et al¹³⁸ were A_s (17.8°C), A_f (33.9°C), M_s (14.2°C) and M_f (-4.0°C).

A careful look at the graphs shown by the authors, shows that the baseline is not satisfactory. M_s and A_s temperatures appear when a sudden change is detected as an increase in the heat flow values. In the same way, M_f and A_f values appear when the values return back to the baseline where they departed from as some authors established²⁰⁴⁻²⁰⁷. The baseline is of paramount importance when dealing with DSC, otherwise it is difficult to establish when a complete phase transformation has been achieved. It would also be difficult to determine whether an R-transition phase is present or not and whether a complete cycle has been reached if the baseline is unclear. An incorrect baseline also leads to rather subjective appreciations of transition temperatures. These are the reasons why the study by Fischer-Brandies et al¹³⁸ has to be used carefully for comparison purposes.

Fischer-Brandies et al¹³⁸ did not detect an R-phase at the CuNiTi wires but they did so at other NiTi they tested. The rhombohedral phase (also known as R-phase) has been observed in many studies on NiTi^{199,201,208,209}.

Although conventionally performed DSC studies like Fischer-Brandies' et al¹³⁸ and Iijima's et al²⁰⁰ were unable to detect R-phase on 35° CuNiTi archwires, Brantley et al²⁰¹ observed it on a constant basis on heating and cooling curves. McCoy²⁰⁸ also observed it on the 35°C CuNiTi wires and Biermann et al²⁰³ also did observe it on the same wires.

It seems that Temperature Modulated DSC used by Brantley et al²⁰¹ may provide greater analysis resolution. This makes that R-phase peaks, which may remain undetected when conventional DSC is performed, arise when TM DSC is used. In any case, other studies that did not perform a TM DSC, found an R-phase on the 35°C CuNiTi wires.

Biermann et al²⁰³ compared as-received CuNiTi archwires (27°C, 35°C and 40°C) to those used in patients by means of DSC. The phase transition temperatures of 27°C, 35°C and 40°C were studied to ascertain if their properties also matched those claimed by the manufacturer.

Biermann et al²⁰³ did not find significant differences among the 35°C CuNiTi as-received wires when heating onset and heating endset results were compared with a variance analysis and Tukey test ($P > .05$). A paired t-test shed no significant differences ($P > .05$) in as-received and retrieved 35°C wires for all parameters (A_s , A_p , M_s , M_f and heating and cooling enthalpy).

This is the reason why for the present research purposes, given that no significant differences of the same manufacturer's have recently been tested and proven, only one archwire has been studied.

There are other reasons for proceeding in this way. Given that manufacturing information is not available, ignoring the origin of the archwires and their exact manufacturing process makes comparisons among groups possible but useless given that differences among them could only be attributed to hypothetical reasons. A basic question like whether the archwires were manufactured from the same coil would be important in order to determine whether that is a qualitatively important issue. The source or origin of what is being under study (the segmented archwires) remains unknown and it is unknown whether the source is the same or not.

Biermann et al²⁰³ concluded that the comparison of measured DSC parameters showed no difference between as-received and clinically retrieved wires, except for a significant reduction in heating enthalpy associated with the martensite-to-austenite transition in the 27°C wires.

The results found at the present research can be analyzed from DSC graphs 27 to 40. Graphs are shown in the same order: as-received specimen, 30 day immersed specimen and the polarized specimen.

Individual measurements of Temperature Transition Ranges yielded the results depicted at tables 15 and 16. Both tables show results obtained from graphs 27 to 38, but different criteria were set for the phase transition temperatures. Table 15 shows results obtained when an absolute or rigid criteria is used, that is, the transition temperature is that value that results from the initial heat flow significant increase (graphs 33 to 38). Table 16 shows results obtained by an often used approximation: the transition temperature would be that one resulting from the intersection between the tangential to the slope of the heat flow sudden increase when it intersects with the baseline temperature (graphs 27 to 32)

Overlapped DSC graphs are shown in graphs 39 and 40 in which different things could be observed.

The martensite to austenite transition of the as-received and potentiostatic polarized specimens basically keeps the same values and no differences could be said to exist. The as-received specimen shows a small peak just before reaching the Af that could be an R-phase as sometimes found by other authors using the modulated DSC. The 30 day and the anodically polarized specimens also show two small peaks after baseline has been reached.

Although conventionally assumed A_s and A_f temperatures according to tangent slopes, it can be seen that absolute A_s and A_f temperatures are quite different. Temperature values once heat flow has completely returned to the baseline indicate that fully obtained austenite phase occurs at higher values. These values label the temperatures at which it could be said with no error that a complete phase has been attained (see data from tables 15 and 16).

Considering again the fact that an R-phase may or may not be present, scientific literature of the materials engineering field suggest that the R-phase may be related to the amount of Cu present at the alloy. Some authors^{210,211} concluded that CuNiTi alloys that contained amounts of copper above 5% wt do not exhibit R-phase. This was in agreement with the results obtained by Brantley et al²⁰¹. So this may be the cause of observing an R-phase but it will later be discussed that small changes in Cu do not yield big changes in transformation temperatures.

The main difference among specimens can be seen at the 30 day immersed specimen. The 50% austenite phase transformation temperature has significantly been moved towards a higher temperature (see graph 39), and an increase in the hysteresis can be declared when looking at the 50% martensite phase transformation temperature which remained unchanged when compared to the other two specimens. According to the obtained results it could be said that the 30 day immersion on a 37°C electrolyte seems to have affected the 50% austenite transition temperature range, meaning that in order to obtain a 50% of austenite phase at the archwire, an increased temperature will be needed. As it can be seen there is also a narrowing at the curve that implies that the austenitic phase is obtained in a narrower range of temperatures. Therefore, martensite to austenite transformation can take place on a narrower range of temperatures in an arch that has been under the effect of the immersion in an electrolyte for 30 days under a 37°C temperature.

This effect should be studied further and thoroughly in order to assert that constant temperature immersion in unloaded arches is responsible of narrowing the martensite to austenite temperature range and increasing the hysteresis.

It does not seem that the observed effect may be due to the fact that the studied arch is different and so it should be attributed to a manufacturing variability of the arches. As it has been said before, sampling is not necessary given that other authors have established that there is no variability among arches of the manufacturer under study for DSC study purposes. Furthermore, Brantley et al²⁰¹ used only two samples because as they proved on a previous study results from replicates were similar. The lack of significant differences among the as-received specimen and the potentiostatically polarized specimen proves that wires of the same manufacturer do not vary significantly.

As-received CuNiTi and potentiostatically polarized specimens got the same DSC results, meaning that induced anodic corrosion, although affecting structurally the wire, leaves a structure that under DSC analyses behaves in the same way. It seems that although a lack of structure results after potentiostatic anodic polarization, CuNiTi wires do not alter their phase transition temperature characteristics. The comparison between the as-received and the polarized specimen is the first reason why it seems that temperature is responsible for the changes observed in the 30 day immersed specimen.

A second reason could be derived from considering again the lack of differences among the as-received and the polarized specimen. The effect of polarization on the CuNiTi surface has to be somehow uniform. Then, polarization seems to affect the surface and the underlying material in such a way that proportions among the alloying elements are kept the same. Otherwise important changes in the phase transition temperatures would be observed. This is thought so, because as Melton et al²¹² proved, varying the alloy composition from 54.5% to 55.% (wt%) nickel causes the M_s temperature to decrease from 57°C to -30°C. Therefore if a non-uniform loss of matter related to the polarization took place, it would be reflected on the phase transition temperatures. In case that variability in the arch composition was suspected to be the reason why a difference was observed at the martensite to austenite transition for the 30 day immersed specimen, this should be discarded as the reason because the austenite to martensite transition should also account for this difference.

A thorough study on CuNiTi alloys done by Gil et al²¹³ also obtained interesting results concerning the relation between composition percentages and phase transition temperatures. The authors found that substitution of large concentrations of Cu does not change the M_s temperature significantly. It was seen that the transformation temperatures, when Cu content ranged from 5% to 10%, were stable in relation with chemical composition changes. For instance, a variation of 0,6% in Ni was seen to produce a M_s change of 0,8°C. And, although M_s was seen to be insensitive to the substitution of Ni by Cu, M_s decreased as Cu substituted Ti. Cu was also seen to make M_s less sensitive to variations in the Ni-Ti ratio. These findings can also be observed for the A_s and A_f values as found by the authors. The authors state that a lower concentration dependent M_s allows for easier production of commercial quantities of materials having a controlled M_s for thermal sensor and actuator uses.

A third and final reason could be derived from the above reasoning. As it has been seen from the SEM, Ni release and AFM tests, 30 day immersed specimens are not dramatically affected by the immersion. The effect that the electrolyte may have on the specimen should be focused on the surface of the specimen and not on the underlying alloy or core of the specimen. So the effect of

the electrolyte is superficial. It is difficult to conclude that a mild effect of the electrolyte on the surface, as the tests resume, may imply a significant change on the martensite to austenite phase transition temperatures.

One of the conclusions reached by Biermann et al²⁰³ was that DSC parameters showed no difference between as-received and clinically retrieved wires, except for a significant reduction in heating enthalpy associated with the martensite-to-austenite transition in the 27°C CuNiTi archwires. In the discussion the authors stated that a decrease in the transformation enthalpy with clinical use would indicate a lessening of the extent of phase transformation and affirmed that although statistically significant, the clinical significance of the reduction in enthalpy is not known at this time.

Therefore, prolonged exposure to temperatures above the A_f temperature should be checked and studied as a factor linked to phase temperature transition temperatures changes, especially when the archwires are under temperatures that are higher than the manufacturers' claim temperature for the A_f value.

Biermann et al²⁰³ found that the A_f of the 27°C and 35°C CuNiTi wires were within approximately 2°C of the manufacturer's claim, which was similar to the A_f found in other studies^{207,208}. Results obtained at the present research show that for an absolute criteria regarding phase transformation temperatures, A_f is far away from 35°C for the as-received sample while is almost 4°C above for the 30 day immersed sample. In case of using an approximation for the A_f value, the temperature is fully reached 3°C under the manufacturer's claim.

Therefore, further studies should be performed to make this point clear and, what is more important, a single reference for transition temperatures measurements should be applied in the same fashion by all researchers, and even the manufacturers' claim should be more clearly stated. Clinical implications around this particular transition temperature of 35°C are quite important because, disregards the criteria used for establishing the transition temperature, a variation of 2-4°C in the temperature could render the archwire useless, and no effect could be accounted for given that the body temperature could be below it.

NiTi

The obtained results for the DSC testing of the NiTi were very reproducible (see graphs 30 to 32 and 36 to 38). Two as-received NiTi wires were DSC tested to see whether a lower temperature limit could be reached under the -100°C working limit. The aim was to obtain a full curve given that, as it can be seen from the graph, the martensite finish temperature could not be reached due to the machine's limit. Although a maximum temperature of -125°C was able to be reached after modifying the DSC configuration, the martensite transformation could be seen but the temperature was not low enough to let the curve stabilize at the baseline.

Although a complete curve could not be obtained, two important conclusions can be drawn. First is that there are no significant differences among as-received wires as far as DSC testing is concerned. The second is that wires have a martensite finish temperature under -100°C which is a pretty low temperature.

A calculation performed by the computers' software confirmed that the areas under both cooling curves shed an enthalpy value equivalent to the heating value at the austenitic transformation.

All tested specimens showed that these wires present a rhombohedral phase prior to the austenitic and martensitic transformation. This is in agreement with other results obtained by several authors^{199,201,208,209}. Leu et al²¹⁴ employed DSC to show that phase transformations were not straight away processes and that they involved an immediate rhombohedral structure as described by Golstein et al²¹⁵ and Otsuka et al²¹⁶.

The heating of the specimens shows the endothermic peaks that belong to the martensite to austenite transformation. As said before, two endothermic peaks have been found for the transformation.

There is an endothermic peak very close to 0°C that according to the scientific literature and actual knowledge²⁰⁹ is the rhombohedral phase (R-phase). More than 50% of the R-phase transformation is attained before reaching the 0°C for all specimens. The endothermic peak for the 50% R-phase shows slight differences toward higher temperatures but they have not been considered to be significant.

The second endothermic peak for the 50% austenitic transformation is also the same for all specimens and the value is 12.5°C with an A_s centered around 6.25°C , the point at which the R-phase is completed. The arches seem to have attained almost a fully austenitic phase at a

temperature close to body temperature (see at the graph the curve values for 37.5°C, line before the 50°C label). Although the phase transformation has almost been reached at body temperature, if the baseline was to be taken as the reference, heating endset values would be found around 42°C-44°C. Heating onset values prior to the R-phase were found to be around -40°C and -41°C when the absolute criteria are used.

The polarized specimen shows a tiny third peak around 25°C. This is supposed to be due to oxides present at the surface of the tested specimen and it is not thought to be a third phase transformation.

The cooling curves also show two exothermic peaks. The first one is an R-phase transformation which is 50% accomplished around 6.25°C which is the temperature at which is the value for the A_s . So this is the first sign of the hysteresis found at the martensite-to-austenite transformation and the reverse transformation from austenite-to-martensite. Martensite start temperature transformation is very far away from the R-phase at the exothermic process. It starts around -62.5°C with an unknown martensite finish value that would be found in a temperature lower than -125°C which was the working limit of the present research. This fact shows that a clear hysteresis of these values would be appreciated when compared with the heating onset values obtained.

A hysteresis can also be found if cooling onset values are compared to the obtained heating endset values. Cooling onset values obtained when baseline is established as reference of the initial heat flow change are comprised between 31°C and 38°C.

Different conclusions could be drawn from the obtained results. Gil et al²¹³ found that small chemical composition changes in NiTi ratios produce large variations in the transformation temperatures for NiTi alloys. For instance, a variation of 0,6% in Ni yields a change in M_s temperature of 11,2°C. Given the fact that very reproducible results have been obtained for the as-received, the 30 day immersed specimen and the polarized specimen, no significant differences in composition of the arches can be seen to exist. Obtained transition transformation temperatures are so similar that a small difference in the Ni-Ti ratios would have been noticed.

The immersion of NiTi in HBSS electrolyte seems to have no impact on the transition transformation temperatures. The effect observed on the CuNiTi specimen could then be closely related to the fact that the wires have been designed for a specific transformation at 35°C or also due to the prolonged exposure to a specific temperature. This hypothesis, as said before, should be thoroughly studied with further research. A link between it and the 'dead wire' phenomenon described by Mallory et al²⁰² on CuNiTi wires should also be investigated.

Martensite obtained temperatures are really low. It can be concluded that the NiTi tested wires are austenitic at room temperature, as values obtained the tangent criteria show, following the results obtained by other studies. This is in agreement with previous studies done by Brantley et al¹⁹⁹. These authors found that five representative commercial NiTi orthodontic wires underwent similar transformations over the temperature range of -170°C to 100°C. They concluded that a martensitic transformation peak with a starting temperature from about -50°C to -80°C may exist in these alloys, but the limit they used was very near to the limit of resolution for the DSC technique employed. They also found that the superelastic NiTi alloys they tested underwent austenitic transformations involving the R-phase which began below 0°C. Their DSC analysis showed that in the oral environment, NiTi was almost entirely austenite.

