

# Degradation of lingual orthodontics archwires

## The effect of corrosion and nickel release on their properties

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## 2. Materials and methods

### 2.1 Materials

#### 2.1.1 The working electrode

Lingual orthodontics archwires are the object of the study. At the present time there is only one manufacturer with a wide variety of materials and cross sections of archwires that makes possible a complete clinical sequence in lingual orthodontics (Photo 1): Ormco's lingual orthodontics archwires (ORMCO Corp., 1332 South Lone Hill Avenue, Glendora, CA 91740, USA)



Photo 1

The archwires chosen for the study were:

1. Respond® 0.0175 inches
2. D-Rect® 0.016x0,022 inches
3. Stainless Steel 0.016 inches
4. Stainless Steel 0.016x0,022 inches
5. Ni-Ti® 0.016 inches
6. TMA® 0.016 inches
7. Copper Ni-Ti® 0.017x0.017 inches

(Although most of them are labelled as ® they will not be labelled as such from now on to make writing and reading easier also at the graphs and figures)

These particular archwires were chosen due to comparison reasons. For instance, TMA of 0.017x0.025 was not chosen because the 0.016 archwire would be supposed to be easily compared to the Ni-Ti and Stainless Steel archwires of the same cross section.

These archwires are manufactured for upper and lower maxilar. Although this fact will not be taken into account at the corrosion testing, it will be kept in mind for the Ni leaching analysis because an estimate for a full mouth appliance will be sought so upper and lower arches will be used and their differences in length and cross section will also be determined to estimate comparable ratios.

### 2.1.1.1 Stainless Steel (SS)

Stainless Steel (SS) is defined as a ferrous alloy with a minimum of 10% chromium content by The American Iron and Steel Institute (AISI). Percentage refers to weight unless noted differently from now on. It may also be found to be described as a ferrous alloy with at least 10,5% chromium by the Stainless Steel Information Centre of the Specialty Steel Industry of North America (SSINA) or 12% as sometimes pointed out by other sources. The fact that the alloy does not rust, stain or corrode as easily as common steel gives the main characteristic of the material. It is also the reason of its known and spread name of stainless or more commonly known inox.

There are different types of stainless steels and they can be grouped in approximately 150 different grades. They are classified according to different categories: metallurgical structure, grade, a particular code (unified numbering system, for example). Among them, there are 15 which are the most common. The information regarding stainless steel and its history that will now be presented was gathered from three sources: the AISI, the SSINA and the Wikipedia websites at the internet<sup>74,75,76</sup>. The study by Sourmail and Badeshia has also been used<sup>184</sup>.

#### 2.1.1.1.1 Introduction and history

In 1821, the corrosion resistance of iron-chromium alloys was first recognized by Pierre Berthier, a French metallurgist. He suggested its use for cutlery due to the good resistance that the alloy exhibited against some acids attack. There have been found different ancient objects made of iron that kept in quite good conditions although being really antique. This is the case of the Iron Pillar of Delhi built and placed by Kumara Gupta I around 400 AD. But, in contrast to iron-chromium alloys studied by Berthier, iron ancient artefacts like the Iron Pillar of Delhi, owed their corrosion resistance and durability to their phosphorous content which was really high and to favourable weather conditions. The passivation layer that formed a protective solid barrier was

then due to both factors: phosphates and oxides.

In 1872, Woods and Clark got a patent for an alloy that had a content of chromium between 30% and 35% and a tungsten content that ranged from 1.5 to 2%.

Three years later, Brustlein studied the importance of carbon levels together with the addition of chromium. It was seen that a level of carbon as low as 0,15% was needed.

Although Berthier recognized the good properties chromium had in the iron alloy in order to protect it against corrosion and Brustlein studied the need of keeping the carbon level low, contemporary metallurgists of that time, were unable to get the proper high chromium and low carbon proportions that characterise nowadays stainless steels, in such a way that the alloy obtained was not too brittle to be able to be used.

In the late 1890's an aluminothermic process was developed by Hans Goldschmidt in Germany that allowed carbon-free chromium production. This fact gave rise to the presentation of the first alloys that could be considered stainless steels during the first decade of the twentieth century.

Leon Guillet published in 1904 his research on alloys with a composition that today fall under the classification of 410, 420, 440-C, 442 and 446.

In 1908, Monnartz and Borchers published the evidence they found of the relation between a minimum level of chromium (10.5%) and the importance of keeping the carbon content as low as possible. They also studied the increased corrosion resistance that molybdenum containing alloys had.

Giesen published in the United Kingdom a broad study on the chromium-nickel stainless steel (austenitic 300 series) in 1909. Portevin did the same, also in France, but with today's 430 stainless steel.

In 1911 Philip Monnartz informed about the relationship of the chromium content of these alloys and their corrosion resistance.

Different industrial developments took place during the first decade of the twentieth century:

1. Erosion resistance alloyed gun barrels. They were being developed at the Brown-Firth

research laboratory (Sheffield, England) by Harry Brearly in 1913. They industrialized a martensitic stainless steel alloy. They patented their chemical analysis in 1919 and most of their work was on 430.

2. Austenitic alloys. Developed by the Krupp Iron Works (Germany) by Eduard Maurer and Benno Strauss with a 21% Chromium and 7% Nickel proportions. They built a famous sailing yacht chrome-nickel steel hull in 1908.

3. Ferritic stainless. Developed at the United States of America by Christian Dantsizen and Frederick Becket.

Although these facts are contemporary, Brearly is most commonly known to be the stainless steel inventor or, in any case, the first to initiate the industrial era of stainless steel.

The fact that stainless steel alloys are resistant to corrosion and staining, relatively inexpensive and that they require a low maintenance and also show a characteristic lust makes them suitable to be applied to a different variety of commercial applications: building material in skyscrapers and large buildings; industrial equipment; cookware, cutlery, hardware; sheets, plates, bars and tubing for civil engineering purposes; surgical instruments and wires of many kinds. The first industrialised use that was given for stainless steel was table cutlery. Another valuable characteristic is the fact that stainless steel is 100% recyclable. It is said that more than 50% of new stainless steel is made of scrap metal melted again.

### 2.1.1.1.2 SS properties

As it is known, iron does not keep its native state as it is extracted from its ore. As soon as it is given the opportunity to react with oxygen present at the environment, it tends to transform into a compound. Rusting is one example of this process of reversion. Chromium can delay the reversion process, and if it is added at large enough concentrations forms a protective layer.

The main characteristic of stainless steel is the fact that resists corrosion quite well. Thanks to the dissolved chromium in solid solution, an invisible surface film is created when the material comes in contact with oxygen. This film is extremely thin, around 1-2 nm thick, and it forms straight away, when oxygen is present. Chromium forms a  $\text{Cr}_2\text{O}_3$  (chromium oxide) layer too thin to be visible and so the alloy keeps its shining aspect. The adherent, coherent and insoluble film blocks oxygen atoms diffusion across the material, protecting the iron from rusting: it is able to insulate the rest of the underlying alloying material which it is not in contact with oxygen. This process is often called passivation.

A passivated material is highly resistant to corrosion. In the case of stainless steel, chromium is the main responsible of this passivation.

Chromium is a highly reactive element and needs to be at least at 10,5% in order to form the passivating film. Increased percentage of chromium gives greater protection properties to the material. Up to 26% of chromium is sometimes used in stainless steels for really harsh environments.

Another characteristic of the film is that it can regenerate itself. For instance, when a scrap is done at the surface of the material, the underlying alloy that has been deprived of the passivating layer quickly reacts with oxygen to form again  $\text{Cr}_2\text{O}_3$ , keeping the remaining underlying alloy protected from corrosion. Passivation can be seen in other metals like aluminium for example.

Other elements are necessary and important to get the best possible chemical properties out of the stainless steels. Other solutes besides chromium are needed to ensure the resistance of the alloy to harsh environments. They normally are carbon, nickel, molybdenum, manganese, silicon, copper, nitrogen, niobium, titanium and sulphur. These solutes allow the possibility of manufacturing a wide variety of alloys that can meet different engineering design requisites depending on the use of the alloy. Nevertheless, most stainless steels are Fe-Cr-C and Fe-Cr-Ni-C alloy based systems, following the historical evolution previously stated which started with a martensitic steel 12Cr-0.1C wt% in the UK and the austenitic 18Cr-8Ni wt% in Germany.

Stainless steels can be classified according to their crystalline structure in austenitic, martensitic, precipitation-hardening martensitic, ferritic and duplex.

The most common crystallographic structures in which iron and its alloys can exist are the body centered cubic (bcc) and the face centered cubic (fcc), shown in figures 1 and 2 respectively.

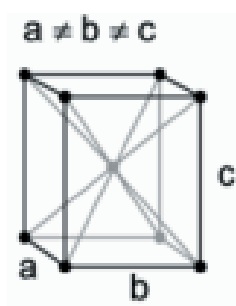


Figure 1

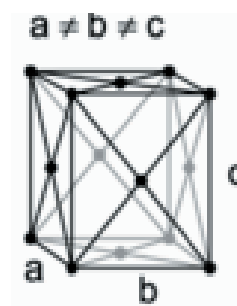


Figure 2

Depending on the alloying system, these crystallographic settings appear in a particular range of temperatures which is nowadays very well known. Pure iron for instance, keeps the fcc structure between 910 and 1400°C, while the bcc structure is obtained below and above this interval, up to the melting point of 1539°C. Therefore iron transforms from a bcc structure to fcc structure called austenite when heated. The fcc structure is a close-packed structure while the bcc structure is not. This explains for example why when this transformation occur the volume of the iron decreases.

This transformation allows a wide range of microstructures to be achieved by heat treatment control. Microstructure determines mechanical properties. A very large range of stainless steels with different strengths, toughness, etc. can be routinely produced with strengths ranging 100 MPa to more than 1 GPa.

Knowledge and control of the relative stabilities of the bcc and fcc structures of iron alloys is therefore of prime concern when manufacturing them.

### 2.1.1.1.3 Types of SS

Figure 3 shows the family tree of stainless steels as presented by SSINA. It is a helpful tool that summarizes the introductory information on SS that follows.

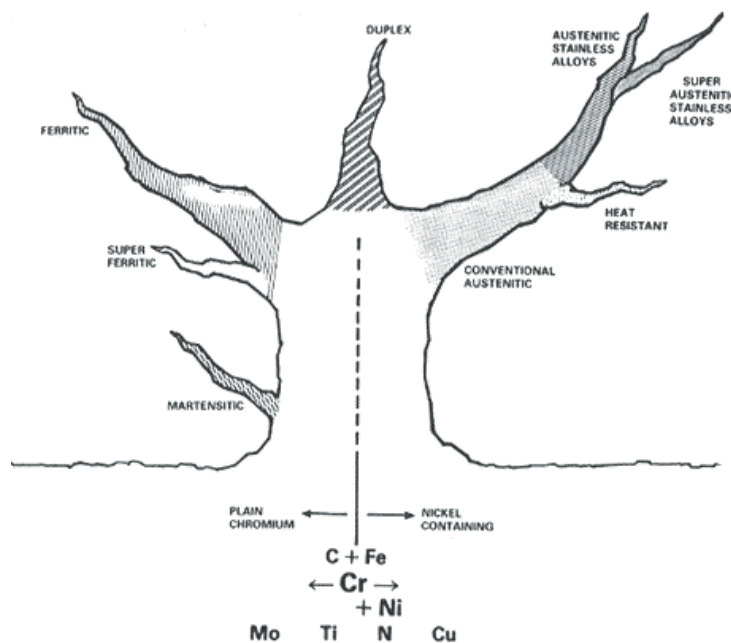


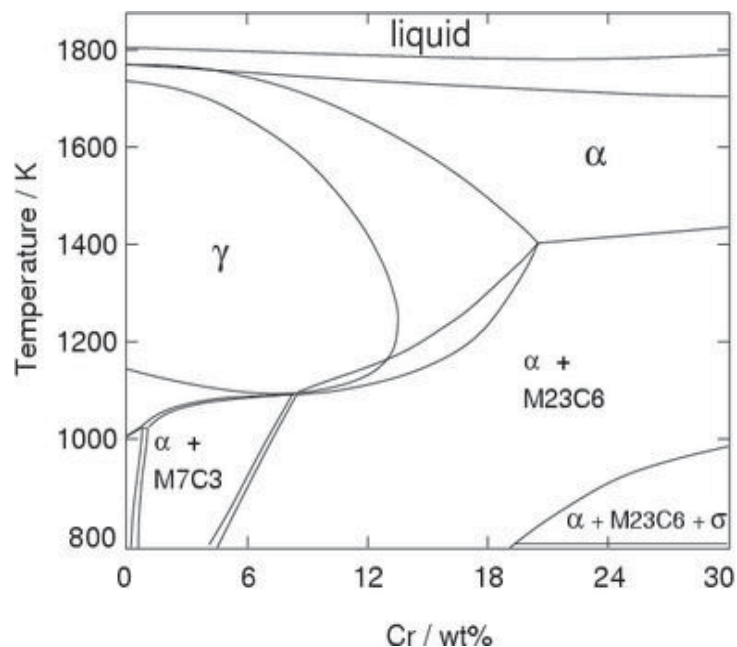
Figure 3

### 2.1.1.1.3.1 Martensitic stainless steels [Fe-Cr-C (Ni Mo) alloys]

High carbon levels are present compared to the rest of stainless steels. Carbon content ranges from 0.15 to 1.20% and chromium is kept between 11.5 and 18.0%. This composition is such that a fully martensitic microstructure at room temperature is achieved. An excessive percentage of chromium can eliminate the austenite phase at all temperatures, avoiding a  $\gamma$  (austenite) to  $\alpha$  (martensite) transition.

Due to the historical reasons that lead the English and German develop different stainless steels, being martensitic and austenitic respectively, depending on the content of Cr and Ni the rest of elements that normally take part in the alloy can be classified as stabilisers of one or the other alloy system.

Elements like Cr which help promote ferrite (alpha, martensitic, bcc) are called ferrite stabilisers. Elements that act like Ni promoting austenite (gamma, austenitic, fcc) are called austenite stabilisers. As it can be seen from the graph 1 being carbon levels as low as 0.1%, austenite no longer forms beyond the limit established around 13.5% chromium. Increasing the carbon content helps stabilising the austenite phase<sup>184</sup>.



Graph 1



The importance of individual elements as stabilisers can be expressed through the following equations when compared with the corresponding effects of Cr and Ni respectively (concentrations in wt%):

$$\text{Cr equivalent} = (\text{Cr}) + 2(\text{Si}) + 1.5(\text{Mo}) + 5(\text{V}) + 5.5(\text{Al}) + 1.75(\text{Nb}) + 1.5(\text{Ti}) + 0.75(\text{W})$$

$$\text{Ni equivalent} = (\text{Ni}) + (\text{Co}) + 0.5(\text{Mn}) + 0.3(\text{Cu}) + 25(\text{N}) + 30(\text{C})$$

Together with chromium, carbon, which is always present, is a key element in stainless steels. As it will be seen, carbon level is kept as low as possible except in martensitic stainless steels. In martensitic, carbon is purposely increased in order to reach high strength and hardness properties. This is done so by high temperature heat treatment, quenching and tempering, developing in this way the martensitic phase.

Austenitisation at a high temperature is a typical heat treatment, and is done in order to dissolve carbides. Quenching is then performed in order to obtain martensite.

Corrosion resistance is very closely related to carbon content. When chromium combines with carbon, forming chrome carbides, a detrimental effect on the formation ability of the “passive” layer is observed. In fact, if chromium is reduced below 10.5%, the passive layer will not form.

Stainless steels manufactured with less than about 0.03 wt% C concentration, compared to the typical 0.08 wt%, are known as low carbon and are designated with an ‘L’ associated with their grade numerical designation (304L and 316L, for instance)

When welding of different parts is to be considered, martensitic stainless steels are a good option given that their low carbon level helps minimize the sensitization risk although this very same condition tends to decrease the yield strength of the material. This drawback is overcome by the addition of nitrogen which helps setting the yield strength back to standard levels.

They can be heat treated to very high hardness, like ferritic stainless steels and they are magnetic too.

### 2.1.1.1.3.2 Ferritic stainless steels [ Fe-Cr (Mo) alloys]

Carbon levels in this type of SS is low, most of them are under 0.12% (442, 446 are at 0.20%). Chromium content ranges 10.5 to 30.0%. They are magnetic. They can not be hardened by heat treatment. Corrosion resistance is particularly good to chloride induced stress cracking (particularly to chloride stress corrosion cracking) but they are not chosen due to their toughness.

### 2.1.1.1.3.3 Austenitic stainless steels [ Fe-Cr-Ni (Mo) alloys]

This iron alloy phase is called after Sir William Chandler Robert-Austen. It is also known as gamma phase iron, is a metallic, non-magnetic solid solution of iron and its alloying element. Its fcc structure has more space than the bcc so it can hold a higher proportion of carbon in solution.

Austenitic stainless steels account for approximately 70% of the total production. They contain a minimum of 16% chromium, being normally in the range of 16.0 to 28.0%. A maximum of 0,15% C is kept although most of them do not get over 0.08% (302, 309 and 310 have slightly higher levels). Enough nickel, between 3.5 and 32.0%, and/or manganese is needed so to keep an austenitic structure under all temperatures comprised from the cryogenic region to the melting point of the alloy, and then a metastable austenitic state is kept for these steels at room temperature and below. Corrosion resistance is highly improved compared to martensitic and ferritic grades due to the addition of Ni although it does not have a direct influence on the development of the passive layer. It results in an increased resistance to acidic corrosion, specially to sulphuric acid.

Most austenitic grades have the martensite start temperature far away from 0°C because, as it is known, martensite can be induced by plastic deformation of austenite and this transformation could be achieved at temperatures higher than the martensite start temperature ( $M_s$ ). There is a temperature though ( $M_d$ ), at which martensite will not be induced no matter how much plastic deformation is applied. This topic will be addressed when introducing the NiTi alloy.

A typical alloy is the 18/10 stainless steel which stands for its 18% chromium and 10% nickel composition. Others like 18/0 and 18/8 are also easily available. The 18/8 is so used that it accounts for approximately the 50% of all stainless steel produced. The basic 18/8 is type 304 austenitic stainless steel.

Other standard stainless steel grades have different studied applications; for instance, type 316 which contains up to 3 wt% of Molybdenum, offers an improved general and pitting corrosion resistance specially to chlorides. This allows it to be the ideal material for marine applications and sea environments and it is preferred over the 304 type. In really harsh scenarios, even type 316 may not be able to withstand the environment conditions and molybdenum-enriched alloys like 254SMO are used.

There are applications like power generator retaining rings and bolts designed to resist very high strength conditions that require an increased strength of the austenitic steels. This is done by controlling the amount of nitrogen added. A quantity as much as 0.4% can be added when the steel is prepared at ambient pressure or a quantity up to 1% can be added if high pressure melting techniques are used<sup>77</sup>. Nitrogen acts as a good solid solution strengthener. Nitrogen atoms do interfere in a static way with dynamic dislocations and they do act as a drag when dislocations are being created<sup>78</sup>. Nitrogen has to be controlled because it can foster chromium nitrides precipitation when used in excessive concentrations. Nickel reduces nitrogen solubility while chromium and manganese increases it.

Resistance to localised corrosion (pitting and crevice corrosion) is also avoided by nitrogen when the austenitic stainless steels are embedded in acid-chloride solutions.

These alloys are non-magnetic and cannot be hardened by heat treatment. They exhibit excellent corrosion resistance and also great ductility and toughness.

#### 2.1.1.1.3.4 Duplex stainless steels [Fe-Cr-Ni (Mo)-N alloys]

They are combined alloys of austenitic and ferritic structures. Carbon levels are below 0.03%, chromium between 21.0 and 26.0%, nickel from 3.5 to 8.0% and they may contain molybdenum up to 4.5% and nitrogen 0.05 to 0.30% These alloys are magnetic and have an increased tensile. Their yield strength is above the other categories.

#### 2.1.1.1.3.5 Precipitation hardening stainless steels [Fe-Cr-Ni (Mo-Cu-Al-Nb)- N alloys]

Carbon levels are under 0.09%, chromium between 12.25 and 18.0%, nickel 3.0 to 8.5%, molybdenum between 2.0 and 2.5% and additions of aluminium, copper, rare earths and nitrogen.

Their ease of manufacturing gives them good corrosion resistance. Structural distortions are minimized due to the fact that high strength is developed at relatively low temperatures (500-800°C).

Table 1 gathers the general information so far presented.

Martensitic								
Grade	C	Cr	Ni	Mn	Si	Mo	P	S
410	0.15	11.5-13.0		1.0	0.5	-	0.04	0.03
416	0.15	12.0-14.0		1.25	1.0	0.60	0.04	0.15
420	0.15-0.40	12.0-14.0		1.0	1.0	-	0.04	0.03
431	0.20	15.0-17.0		1.0	1.0	1.25-2.0	0.04	0.03
440A	0.60-0.75	16.0-18.0		1.0	1.0	0.75	0.04	0.03
440B	0.75-0.95	16.0-18.0		1.0	1.0	0.75	0.04	0.03
440C	0.95-1.20	16.0-18.0		1.0	1.0	0.75	0.04	0.03

Ferritic								
Grade	C	Cr	Ni	Mn	Si	Mo	P	S
405	0.08	11.5-14.5		1.0	1.0	-	0.04	0.03
409	0.08	10.5-11.75		1.0	1.0	-	0.045	0.045
429	0.12	14.0-16.0		1.0	1.0	-	0.04	0.03
430	0.12	16.0-18.0	0.75	1.0	1.0	-	0.04	0.03
446	0.20	23.0-27.0		1.5	1.0	-	0.04	0.03

Austenitic										
Grade	C	Cr	Ni	Mn	Si	Mo	Ti	Nb	Al	V
301	0.15	16-18	6-8.0	2.00	1.00					
302	0.15	17-19	8-10.0	2.00	1.00					
304	0.08	17.5-20	8-10.5	2.00	1.00	P:0.045	S:0.030			
310	0.25	24-26	19-22	2.00	1.50					
316	0.08	16-18	10-14.0	2.00	1.00	2.0-3.0	P:0.045	S:0.030		
321	0.08	17-19	9-12.0	2.00	1.00		5 x %C min.			
347	0.08	17-19	9-13.0	2.00	1.00			10 x %C min.		
E 1250	0.1	15.0	10.0	6.0	0.5					0.25
20/25-Nb	0.05	20.0	25.0	1.0	1.0			0.7		
A 286	0.05	15.0	26.0	1.0	1.0	1.2	~1.9	~0.18	~0.25	
254SMO	0.02	18.5-20.5	17.5-18.5	1.0	0.8	6-6.5	~1.9	~0.18	~0.25	
AL-6XN	0.03	20-22	23.5-25.5	2.0	1.0	6-7.0				

Duplex								
Grade	C	Cr	Ni	Mn	Si	Others	P	S
Type 329	0.10	28.0	6.0	2.0	1.0	1.5 Mo	0.04	0.03
Type 326	0.05	26.0	6.5	1.0	0.6	0.25 Ti	0.01	0.01
2RE60	0.02	18.5	4.5	1.5	1.6	2.5 Mo	0.01	0.01
IC378	0.03	21.8	5.5	1.38	0.40	0.07 Mo 0.18 Cu 0.07 V 0.14 N	0.03	0.01
IC381	0.02	22.1	5.8	1.92	0.48	0.2 Mo 0.17 Cu 0.13 V 0.14 N	0.03	0.01
A219	0.03	25.6	9.4	0.70	0.60	6.1 Mo 0.27 N	0.02	0.01

Table 1

### 2.1.1.1.4 SS in orthodontics

The use of stainless steels in orthodontics started thanks to the advances in the industrial processes that allowed different kind of sections to be manufactured. World War I necessities gave rise to industrialized drawing processes that allowed the manufacture of wires in the late 1930s. Deformation was achieved by pulling the material through a die thanks to a tensile force applied at the exit of the die. This gave way to manufacturing wires and tubes.

Around the 1950s most orthodontic appliances were being made of type 300 series stainless steel alloys. Due to the improved industrialised drawing processes that allowed small cross-sectional wire areas to be made, gold archwires that had been used so far, lost favour to the stainless steel wires. At the end of the 1950s two tempers of cold worked wires were being offered by Rocky Mountain Orthodontics: a standard grade and an extra hard.

In contemporary medical practice the most used stainless steel alloy is AISI 316L type. Although AISI 304 type is more prone to corrosion due to its lack of molybdenum compared to the 316L, most stainless steel archwires produced for orthodontics are of this type. They are more affected by pit corrosion than 316L.

A recent study by Verstrynge et al<sup>32</sup> presented a wide revision of the stainless steel most commonly used archwires in orthodontic practice and found that over the ten stainless steel wires studied, nine were AISI 304 type and only one was a nickel free (0.10% Ni) stainless steel ASTM F2229 (23% Mn, 21% Cr and 1%Mo) which was the Noninium wire made by Dentaureum (Ispringem, Germany).

Due to the fierce competence that is present among manufacturers, wire compositions are not normally given or published by manufacturers. The study of Verstrynge et al<sup>32</sup> sheds a new light on this well kept secret. Their findings have been adapted and are shown in table 2.

	18 Cr, 8 Ni, 2 Mn, 1 Si (0.08 C)	23 Mn, 21 Cr, 1 Mo (0.10 Ni)
1 3M	x	
2 TP Orthodontics	x	
3 Ormco	x	
4 G&H Wire Company	x	
5 Ortho Organizers	x	
6 GAC	x	
7 3M Unitek (Hi-T II)	x	
8 Rocky Mountains Orthodontics Europe	x	
9 American Orthodontics	x	
10 Dentaureum		x

AISI 304

ASTM F2229

Table 2

## 2.1.1.1.5 SS wires of this study

The stainless steel wires used in the present thesis are:

Respond (0.0175 inches)

D-Rect (0.016x0.022 inches)

Stainless steel (0.016x0.022 inches)

Stainless steel (0.016 inches)

Photos 2 to 5 respectively show the ss archwires



Photo 2



Photo 3



Photo 4



Photo 5

### 2.1.1.1.5.1 Respond

It is a braided wire of round section. At present time, in lingual technique, it can be found in two different sections from Ormco: 0.0175 and 0.0155 inch.

It is used as first wire in patients with very crowded teeth and also in highly misaligned teeth. It is a very comfortable wire for patients given that the engagement force and the delivering force is very low. It has low resistance to permanent deformation and that implies that it does not remain active in mouth when engaged for a long time, especially if initial crowding and misalignment is severe. It only starts a mild alignment and levelling and it is not able to correct rotations. Low pain tolerance levels and periodontal disease are indications for this wire to be the first one to be engaged even in case that previous stated indications were not present.

Respond archwire has to be replaced very soon after engagement and it therefore does not remain in mouth such a long time as other wires. As soon as the patient gets used to the wire and the patient is not uncomfortable with it, the archwire should be replaced and the treatment sequence should proceed.

### 2.1.1.1.5.2 D-Rect

It is also a braided wire but it has a rectangular section of 0.016x0.022 inches. The engagement and delivering force to teeth is a bit higher compared to the Respond. It has the same indications as the previous wire but given its rectangular section it can establish, at least initially, a torque correction.

### 2.1.1.1.5.3 SS 0.016x0.022

When levelling, alignment and rotation corrections have come to its close, and initial torque has been established, rectangular wires like this one can be engaged. They are especially suited for torque corrections. Space closure can be easily performed with this wire given its low friction coefficient. Arch form consolidation can be also performed with this wire. It remains in mouth also for a relatively long time compared to the initial braided stainless steel wires.

#### 2.1.1.1.5.4 SS 0.016

It is a round section wire. Many times it can be used as first wire when initial crowding and misalignment is not so severe and the patient can withstand the engagement force and the delivered force to the dentition. Most authors like Echarri<sup>79</sup>, Scuzzo and Takemoto<sup>6</sup>, recommend the use of this archwire to perform the initial canine retraction or levelling before engaging a full appliance. Bendings can be done on it in order to accomplish retraction purposes without compromising premolars in anterior levelling, alignment and distalization according to different biomechanic strategies. They are also used in the last stages of treatment when consolidating the dentition. Given their mechanical characteristics (deformation) it has to be taken into account that it is not recommended to proceed with an engagement step that implies a wire deflection bigger than 1 mm due to the fact that a patient will not be able to withstand it or, anyway, because root resorption or hialinization could be caused. Distance ligatures are then indicated. They are suitable for all kind of bendings. This wire remains active more time than the braided stainless steel wires.

Part and lot numbers of archwires used are as follows:

Archwire	Part number	Lot
Respond	203-0007	05G18
D-Rect	201-0023	04H206H
SS 0.016x0.022	206-0006	05J84
SS 0.016	206-0001	05E5

#### 2.1.1.2 Nickel-Titanium (NiTi) and Copper-Nickel-Titanium (CuNiTi)

##### 2.1.1.2.1 Introduction and history

At the end of 1960s, alloys with shape memory effect were being studied and tested at the military field to see which applications could be given to them<sup>80,81</sup>. Among the different alloys, there was one made of nickel and titanium that was named NITINOL after Nickel-Titanium Naval Ordnance Laboratory.

As some of the achievements in medical applications like x-rays and penicillin, NiTi



properties were discovered by accident. At the Naval Ordnance Laboratory, researchers pounded by hammering some NiTi samples. The aim was to determine the force necessary to induce deformation. The researchers left for lunch and when they got back to the laboratory discovered that the deformations had been 'repaired' themselves.

In the same way that Stainless Steel history has been presented as a way started from different points in order to achieve a stainless alloy, the Nickel-Titanium alloy history relies on the efforts of developing a shape memory material, with two properties combined: pseudoelasticity and thermoelasticity, which so far had not been found in any alloy. Researchers were looking for a material that could undergo a force induced phase-transformation when the material temperature was increased to a desired point.

One of the features that this alloy presented was the fact that could be deformed, clamped, heated and cooled to give a specific shape. The material, once deformed to a new shape and heated could get back to its initial post-heat treatment shape<sup>82,83</sup>.

The historical evolution takes us back to the early 1930s. Otsuka and Wayman<sup>84</sup> reported that pseudoelastic behaviour was discovered by A. Ölander in 1932 while studying the Au-Cd alloy. In 1938, the effects of decreasing and increasing the temperature over the formation and disappearance of the martensitic phase when studying a Cu-Zn alloy were first observed by Greninger and Mooradian<sup>85</sup>. Kurdjumov and Khandros<sup>86</sup> in 1949 followed by Chang and Read<sup>87</sup> in 1951 reported the phenomenon of the memory effect governed by the thermoelastic behavior of the martensite phase.

Since Buehler et al<sup>80,81</sup> and his co-workers discovered the NiTi alloy properties there have been many investigations trying to explain the mechanical behaviour of the alloy. Applications did not arrive too late. According to Castleman et al<sup>88</sup>, the first efforts to use the new alloy as a biomaterial seem to have been made by Johnson and Alicandri in 1968 as an implant material.

The first medical applications were first reported in the 1970s by several authors<sup>88-91</sup>. The widespread use of the alloy as a medical application has been due to the stent device in cardiovascular surgery that can be considered the breakthrough of this alloy in medical applications, which occurred during the mid 1990s. Nitinol was introduced in the late 1980s in minimally invasive endovascular surgical procedures. Although it was seen to be more expensive than stainless steel, it was a good alternative to the expandable balloon devices due to the self expanding properties as a response to body temperature exposure. Compared to the contemporary alloys, NiTi was surprising due to its shape memory effect and superelasticity, both new properties so far not

found.

The first NiTi consumer commercial application for the alloy was focused in coupling pipes both for house and the industrial field.

Shape memory alloys research lead to the development of basically three different alloy systems: copper-zinc-aluminium, copper-aluminium-nickel, and nickel-titanium alloys. Although more expensive, NiTi alloys have superior physical properties when compared to the copper based alloying systems.

### 2.1.1.2.2 NiTi and CuNiTi properties

NiTi alloys manufacturing is a double melting process done in vacuum so to obtain a high quality and purity product and obtain the desired properties. When raw materials are obtained (it consists of an equiatomic mix of Ni and Ti), they are melted by induction at 1400°C, which is the first melting vacuum stage of the process. At this step, the transition temperature has to be controlled very well because small changes in the alloy chemistry composition give as a result a big variation in the transition temperature. The importance of transition temperatures will be explained later. When transition temperature has been under control, alloy re-melting under vacuum arc helps improving the structural properties of the alloy. The resulting alloy can be hot worked at 800°C and cold worked to obtain different products of a wide range of sizes and shapes<sup>92</sup>.

NiTi could be compared to stainless steel in the sense that it presents a surface layer which is different in composition from the underlying alloy. In the case of the NiTi alloy, oxide layer thickness varies over a bigger range than the stainless steel one, being 2- 20 nm.

Titanium oxides (TiO<sub>2</sub>) and nickel oxides in a smaller quantity (NiO and Ni<sub>2</sub>O<sub>3</sub>) are the main surface components according to different authors<sup>92-99</sup>.

In any case, the layer thickness of the oxide layer and its chemistry will vary depending on the manufacturing method and the surface treatments that could be done on it. For instance Trigwell et al<sup>100</sup> showed that the amount of Ni could change due to the above mentioned factors over a wide range.

Oshida et al<sup>94</sup> discovered an interesting fact. According to them, nickel dissolves more easily due to the fact that its oxide seems to be more unstable than the titanium oxide. This selective

nickel dissolution would be the explanation of the long island-like structures that features the irregular surface of the alloy in the wires these authors studied. It should be noted that this finding applies to surface of untreated NiTi.

When referring to treated surfaces by mechanical polishing, boiling and autoclaving, noticeable differences were found by Shabalovskaya<sup>97</sup>. Ti/Ni Ratio increased to 5.5 when the specimens were mechanically polished compared to the untreated specimens, and increased up to a range of 23.4-33.1 when the specimens were treated by boiling and autoclaving. Similar results were found by Hanawa<sup>93</sup>. He observed that Ti/Ni ratio got to 5.8 with polishing and increased to 91 by simply immersing the specimens for 30 days in a neutral electrolyte solution.

Biocompatibility is one of the main characteristics of titanium and some of its alloys. It is thought that good biocompatibility relies on the stability of the titanium oxide layer. When implants are considered, it is known that the oxide layer is able to take up minerals and other biofluid components and this reaction causes a change in the surface of the material allowing the bone to grow touching the implant and stabilizing it. Although the present thesis does not cover dental implants, it should be noted that Ti and NiTi are mostly known among the general public mainly due to biocompatibility they present.

As it has been previously stated, the main properties of this alloy are shape memory effect (SME), pseudoelasticity and thermoelasticity.

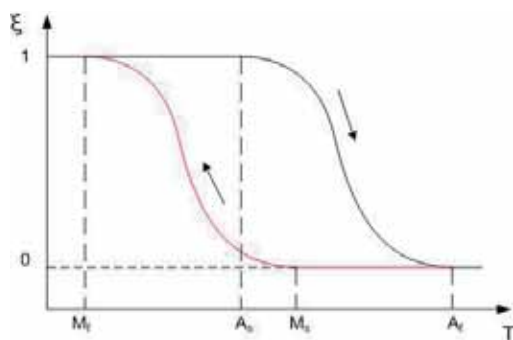
### 2.1.1.2.2.1 Temperature effect

In NiTi shape memory metal alloys, there are two different temperatures and loading dependent crystal structures (phases): martensite (lower temperature) and austenite (higher temperature or parent phase). Properties of austenite NiTi and martensite NiTi are notably different and therefore they will be applied to different uses.

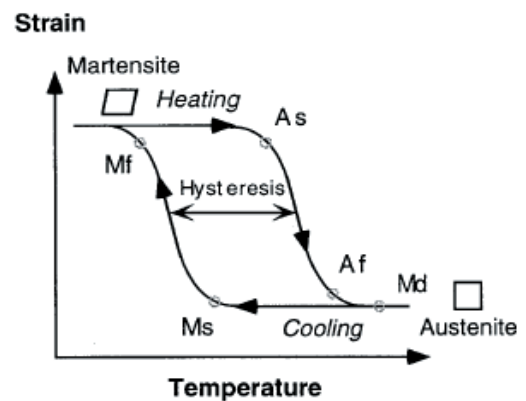
Upon heating, NiTi martensitic crystal structure changes into austenite. The temperature at which phase transformation begins is called austenite temperature start ( $A_s$ ), and the transformation is complete at ( $A_f$ ), austenite finish temperature. When cooling, a martensite transformation is seen and the start and finish temperatures for this phase are respectively known as  $M_s$  and  $M_f$ . These temperatures are sometimes referred as phase transformation temperatures or transition temperatures. As stated before, composition, surface and metallurgical treatments have an important impact on these temperatures.

Taking into account the practical application towards which the alloy is being designed, three NiTi forms can be found: martensite, stress-induced martensite (also known as superelastic) and austenite. The phase of the alloy is designed for a specific range of temperature depending on the sought effect. Martensite is ductile and soft and it is easily deformed while austenitic is strong and hard. Stress-induced martensite is highly elastic.

Temperature-phase transformation relationship can be seen at graph 2<sup>101</sup> and temperature-phase transformation linked to strain at graph 3<sup>102</sup>.



Graph 2



Graph 3

Both graphs show temperature influence on alloy phase. As it can be observed in graph 2, martensite ( $\xi$  refers to full martensite: 1, full austenite: 0) transforms into austenite by heating. Transformation starts at  $A_s$  temperature and finishes at  $A_f$ .  $A_f$  is typically 2 to 20 °C or hotter than  $A_s$ , depending on the alloy or the loading conditions.  $A_s$  is determined by the alloy type and composition, and it can be varied between -150 °C and maximum 200 °C.

On the way back to martensite by cooling, phase transformation starts occurring at a higher temperature. The difference in start temperatures when phase transformation is done from martensite to austenite compared to austenite to martensite transformation is called hysteresis. It is formally defined as the temperature difference between the 50% transformation from martensite to austenite and viceversa. At the above graph temperature values should be looked for when  $\xi = 0,5$ .

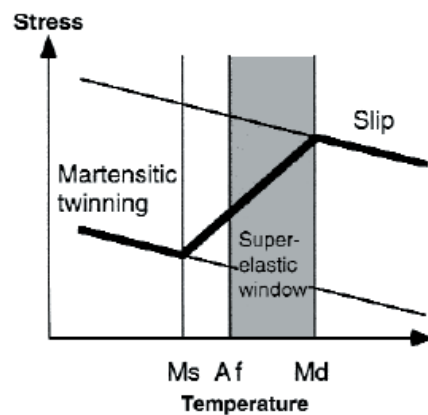
According to Buehler et al<sup>81</sup> and Funakubo<sup>103</sup> hysteresis could be between 20 and 30°C, but other sources say that it could vary between 30 and 50°C<sup>102</sup>. This implies that if an alloy is meant

to be fully transformed into the austenitic phase when heated by body temperature,  $A_f$  has to be close to  $37^\circ\text{C}$ . Then,  $M_f$  will be around  $5^\circ\text{C}$  to fully obtain the martensite phase.

The manufacturing method can establish different  $A_s$  and  $A_f$  temperatures depending on the applications that are sought.

Temperature Transformation Range (TTR), that is the temperature difference where phase transformation can be observed or the temperature difference established by  $M_f$  and  $A_p$  can be established between  $-200^\circ\text{C}$  to  $110^\circ\text{C}$ . It is a quite wide spectrum but it should be taken into account that the closest that the TTR gets to the ends of this spectrum, the more expensive the raw materials and manufacturing processes are. These resulting alloys are more difficult to work with and it is difficult to obtain consistent results with them. The transformation range is thought to be in agreement with the operating temperature of the alloy or else shape memory effect will not be present.

Once  $A_f$  is attained, if stress is still increased austenite gives way to stress induced martensite where superelasticity (or pseudoelasticity) can be observed. This temperature range starts at  $A_f$  and finishes at a point labelled as  $M_d$ , and it is called the Superelastic Range. At this range, the increase of stress increases the yield point strength of the material linearly (graph 4)



Graph 4

TTRs can be varied by slight changes in their Ni/Ti ratio or by adding cobalt and nickel instead of them.  $A_f$  can be decreased by Ni addition. When the Ni weight is above 55.6% the NiTi SME and pseudoelasticity disappear no longer being qualities belonging to the alloy. This is due to the formation of a  $\text{Ti-Ni}_3$  phase which is very stable. The addition of Cobalt is able to a certain extent to lower again the TTR.

Functional fatigue can also shift transformation temperatures of an alloy. The repeated use of the shape memory property is related to a change of microstructural and functional properties of the material. Short-term temperature changes can also affect archwires' mechanic characteristics as shown by Meling et al<sup>104</sup>.

Heat treatment, with differences induced by time and temperature, can also greatly modify NiTi properties<sup>81</sup>.

The temperature dependent phase transformation is usually referred to as thermoelastic martensitic phase transformation. This is a unique property when comparing NiTi to other alloys. This temperature induced transformation is linked to a shape change as it can be deduced from graph 3. It is thought that the fact that things tend to accommodate to the minimum energy state for a given temperature is the reason why the crystal lattice structure changes<sup>84</sup>.

Martensitic phase is characterised by being the lower temperature phase, the phase where the alloy is ductile, soft and can easily be deformed. This is explained by its crystal properties. When cooled below  $M_p$ , martensite can be obtained in a variety of 24 relative orientations or variants, so symmetry in this phase is not very high. At this point, a complex rhombic structure can be found. When the alloy is heated above  $A_f$  there is only one crystal configuration that is achieved, no matter what the initial martensite crystal configuration or variant was. The austenite phase is very symmetric and it is a simple cubic structure. According to Andreasen et al<sup>92</sup> and Gil et al<sup>105</sup> this fact helps to understand the specimen complete reversion to the shape previous to deformation.

Shape memory effect can present a one-way or a two-way change.

SME is the reason why NiTi alloys are sometimes popularly known as smart materials. These alloys are able to notice temperature changes around room temperature and they react by converting its shape to a pre-set or pre-programmed shape. The shape change induced by temperature from martensite to austenite by heating is known as a one-way change. In case that after being heated and transformed to the austenite phase, the alloy still remembers its martensitic phase form after cooling, this change is referred as a two-way change.

Figure 4 shows these kinds of shape memory effects.

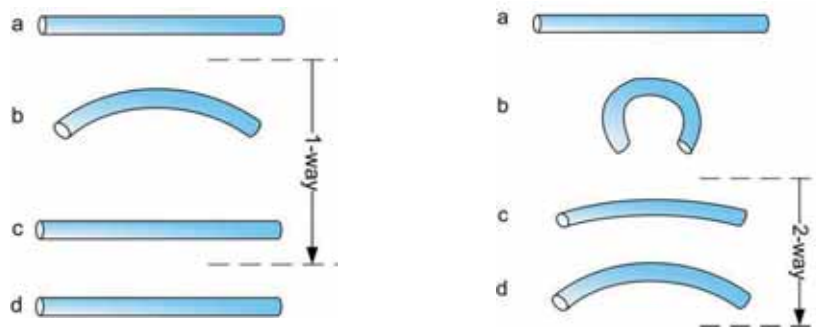


Figure 4

### One way and two way effect

- a. Starting from martensite.
- b. Adding a reversible deformation for the one-way effect or severe deformation with an irreversible amount for the two-way.
- c. Heating the sample.
- d. Cooling it again.

As it can be seen at the one-way effect, when cooling from high temperatures the sample does not undergo a macroscopic shape change, it remains unchanged. A deformation is necessary to create the low-temperature shape in case it was needed. So, although upon heating the alloy resumes its original shape and rigidity, once cooling is applied, low-temperature shape is not recovered.

At the two-way shape memory effect the material remembers two different shapes: the low temperature shape and the high temperature shape. Unlike this force induced memory effect there could be an intrinsic two-way effect which would not be induced by the application of an external force. It can be seen that, although the lower temperature shape is not fully recovered, the sample tends to it. Two-way memory is quite exceptional, but all-round shape memory effect, which is a special case of the two-way shape memory effect, has been described by some authors<sup>106</sup>.

NiTi alloys can be 'trained' or 'programmed' to behave with a two-way effect.

Training is the reason why the material behaves differently. The high temperature shape can be remembered by the alloy. But once it has been heated some alloys forget the low temperature shape. In order to be able to recover the low-temperature shape the alloy has to be trained.

### 2.1.1.2.2.2 Force effect

Twinning is the mechanism by which martensite phase deforms. When crystal structure is looked at, it can be observed that, being the reference a particular atom plane, deformation undergoes like a mirror symmetrical displacement. The atom plane that is established as reference is called the twinning plane<sup>81,92</sup>.

Conventional materials like stainless steel deform in a very well known manner. Upon loading, the material deforms following a stress/strain ratio known as modulus of elasticity (or Young's Modulus) which may vary according to the material properties. The modulus is the slope of the stress to strain line described on a graph. The material deforms in a predictable manner until a particular strain has been reached, called the tensile yield strength point. Up until that point, if the material is unloaded, it will fully recover its initial shape. The deformation that has been applied is reversible and it is said to follow Hooke's law of deformation, and due to the ability of the material to recover the shape, that kind of deformation it is called elastic. Loading passed the yield strength point will result in plastic deformation, meaning that if unloaded, the material will not fully recover its original shape and there will remain a deformation that is proportional to the point in which unloading was undergone. This kind of deformation is referred as plastic deformation. When materials have a yield point they are said to be ductile. There are materials that do not have a yield strength point and simply fracture when load reaches a certain level. They are then referred as being brittle.

Ductile materials, after the yield point is reached, present dislocations in a way called slip dislocations shown in figure 5.

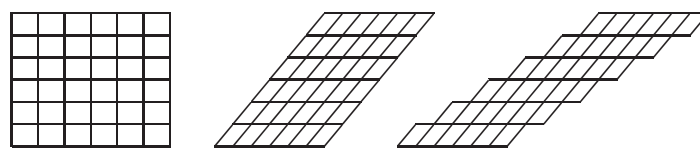


Figure 5

Crystal lattices glide along each other changing the overall initial geometry of the material as it can be seen from figure 6. Lattice properties will give rise to, different slip systems.





Figure 6

When pressure is applied at the low temperature phase in shape memory materials, atoms arrange themselves in a relative orientation so to accommodate the pressure that is being applied. Unlike most metals, NiTi responds to applied forces by changing the crystalline orientation at the twin boundaries, and does not undergo slip deformation or dislocation as most metals do (figure 7)

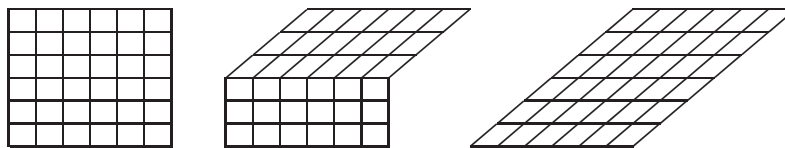
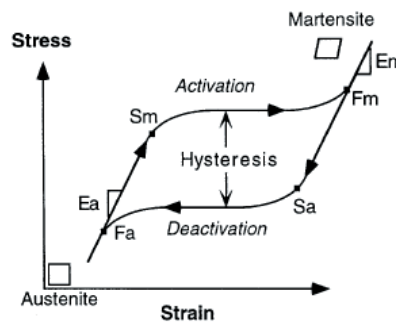


Figure 7

Stress-Strain diagram for the alloy does not follow the standard Stress-Strain graph that follows Hooke's law. Duerig and Zadno<sup>101</sup> presented a graph similar to the one labelled as graph 5.



Graph 5

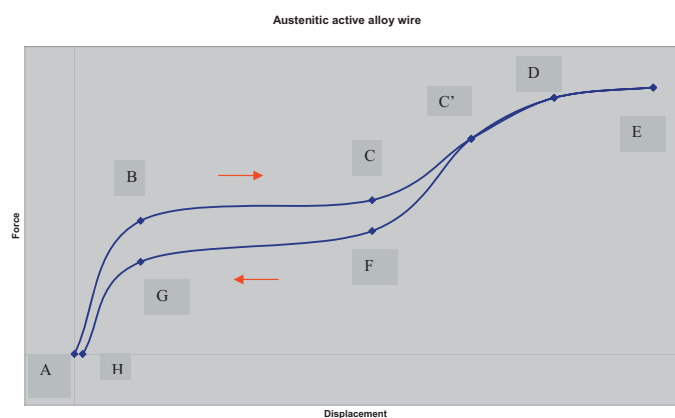
As it can be observed, a special region is found after martensitic transformation starts followed by an increase of stress. The linear increase in the strain due to stress applied (or viceversa) gives

way to a region where stress does not increase although strain keeps increasing. This plateau-like area is due to the formation of martensite induced by stress (SIM). Austenite to martensite and martensite to austenite transformations do not follow in the stress-strain relation the same path. Hysteresis is also found in this transformation as previously described for other graph. Activation and deactivation plateaus present different stress magnitudes. This phenomenon is clinically very beneficial because it implies that the delivered force will be lighter than the activation force for the same strain.

NiTi has another property which is different from commonly used metallic alloys. It is a superelastic alloy. Superelasticity (or pseudoelasticity) is the property by which some materials are able to recover the original shape after a substantial deformation that exceeds the commonly set limits for hookian elasticity. Strains up to 10% can be applied to superelastic materials and the material will be expected to remain in the range of a reversible deformation.

The region where the phenomenon takes place is pseudoelastic and it is only found in a particular range of temperatures as showed in graph 4.

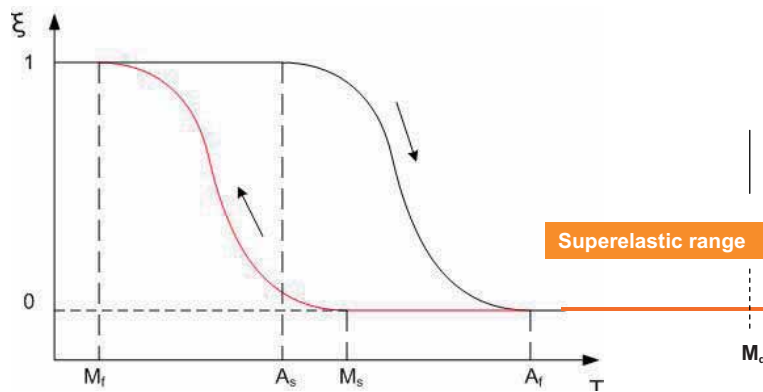
Pseudoelasticity also has some limits. Unloading and heating will only be able to recover around an 8% of strain. If the alloy is overstrained above this value, permanent plastic deformation is established. When overstrained, the alloy is not able to keep a correspondent variant to the austenitic phase, so classical plastic deformation is observed by the commonly known slip effect. Then this deformation is not recoverable and obviously it can be said that memory effect and pseudoelasticity has been lost. This can be also seen at graphs 4 and 6.



Graph 6

In order to understand superelasticity from a microstructural point of view we should go back to two previously shown graphs (graphs 2 and 3)

As it can be seen a new region has been added in graph 7 that it was not previously introduced.



Graph 7

At temperatures higher than  $A_p$ , there is a region where, at a given temperature, the applied load is able to induce a new phase, which curiously is martensitic. It is called SIM. The applied load is absorbed by the alloy by shifting to a martensite phase. The highest temperature that will allow SIM formation will be that labelled by  $M_d$ . Allowed strains, when compared to commonly used metals, are much higher before being plastically deformed, showing a rubber-like behaviour over a specific temperature range that goes from  $A_f$  to  $M_d$ . When temperature goes above  $M_d$  the alloy will undergo the typical slip non-reversible deformation. The closer to  $A_f$  the load is applied, the easier the material will recover the initial shape once unloading is produced<sup>107</sup>.

Duerig and Zadno<sup>101</sup> summarized it as shown in graph 4. As it can be seen, martensitic twinning takes place at temperatures under  $M_s$ . SIM appears at temperatures that fall between  $M_s$  and  $A_p$ , and once induced, SIM is stable. When temperatures go above  $A_p$ , SIM becomes unstable during unloading and superelasticity is observed. The region comprised between  $A_f$  and  $M_d$  can be known as the superelastic window. Therefore, superelasticity is present only in a particular range of temperatures.

Programming one and two-way shape memory effect is as follows:

One-way shape memory effect needs the NiTi sample to be molded with the needed shape. This is followed by a heat treatment in order to set the final shape. Variance in temperature and time will be introduced according to the properties of the alloy<sup>84</sup>. Rapid cooling is most times looked for either by rapid air cooling or water quenching.

Two-way effect programming can be achieved by SME or SIM methods.

SME consists of cooling the sample below  $M_f$ . At that stage the desired shape is given and it is heated above  $A_f$  letting it take its austenite phase shape. This is done for 20 to 30 times to get fully trained sample. The sample will have a programmed shape for temperatures under  $M_f$  and another for above  $A_f$  temperatures.

SIM is done by achieving a temperature just above  $M_s$  at which the sample is bent to obtain SIM preferred variants. It is subsequently cooled under  $M_f$  temperature. When heated above  $A_p$ , the sample will be able to recover its original austenitic shape. This is also done for 20 to 30 times.

### 2.1.1.2.3 NiTi and CuNiTi in orthodontics

The introduction of NiTi as an alloy for archwires manufacturing has been one of the main advances in dentistry. It is known by all that light and continuous forces are the ideal type of forces when tooth movement is wanted.

These properties are somehow limited by the cross-section of the archwires which are also closely related to the bracket slot. In case that either cross-section or bracket slot dimensions were considered to be fixed values there would not be other way of addressing the search of new mechanical properties than looking for new materials, especially alloys. If there was a slight freedom for archwire cross-section or bracket variability that would not be big enough in order to get significantly different mechanical properties with the same materials. Therefore the need of research for new materials has always been present.

George F. Andreasen was the first dentist that recognized the future uses that the NiTi alloy could have in orthodontics. This occurred while reading a supplement of the Journal of American Orthodontics called the United States Naval Laboratory publication around 1969. It took seven years of research before the formula was formally presented as a patent (n° 4.037.324) on the 26<sup>th</sup> of July of 1979. This patent was introduced in the orthodontic market through the Unitek Company and it was called Nitinol®.

Although the new alloy was introduced as a SME material, its equiatomic NiTi composition did not yield the sought effect. Cold working during the drawing manufacturing process to more than 8 to 10% had suppressed the SME rendering it passive<sup>108</sup>. Although passive, in the martensitic stabilized condition, the alloy was really attractive for clinical use. It was seen that it had a very

low stiffness, that is, very low force per unit of deactivation<sup>109</sup>. It better met the ideal low and continuous force delivering properties compared to its competitors. It was seen that it was a really springy archwire that delivered only one-fifth to one-sixth of force per unit of deactivation. It was also seen that the increment of deactivation was followed by the same loss of force, meaning that the stiffness was linear as that of a spring. All its predecessors at the orthodontic market also showed this characteristic<sup>110</sup>.

Once it was discovered that the initial alloy composition was passive, an active alloy was looked for in order to take advantage of the SME and pseudoelasticity of the material: the austenitic active alloy and the martensitic active alloy.

Although some authors had previously given general values for NiTi in both phases, other authors<sup>110-113</sup> have really focused on the Nitinol<sup>®</sup> obtaining the following values:

#### Martensite

Elastic modulus = 31-35 GPa

Ultimate strength = 1.4-1.7 GPa

#### Austenite

Elastic modulus = 84-98 GPa

Ultimate strength = 0.84 GPa

It should be remembered that stainless steel archwires values are around the following:

Elastic modulus = 200 GPa

Ultimate strength = 2.1 GPa

The austenitic active alloy force-displacement behaviour can be described as previously shown in graph 6 as adapted from a reference<sup>114</sup>.

When engaging the archwire trying to get it through the slot of two brackets that are placed in teeth that are misaligned, not levelled still, the arch is said been loaded. In other words, the arch is subjected to a certain deflection that is forcing it away from its initial contour shape.

At the present case, the austenitic active alloy wire starts a stiffness response that would be

around three times that of the conventional martensite passive alloy (A-B). This short-lived effect is followed by a plateau-like area in which a wide displacement range can be obtained while the force is kept constant (B-C). All the way from A to C, austenitic phase is being shifted to martensitic phase

Once the austenitic phase can no longer withstand a given displacement keeping a constant force there comes into play a phase transformation to the martensitic phase (SIM). It can be observed that the reoccurring positive slope is a third of the value of the initial A-B leg, so stiffness is seen to be reduced. The C-E region is a martensitic region.

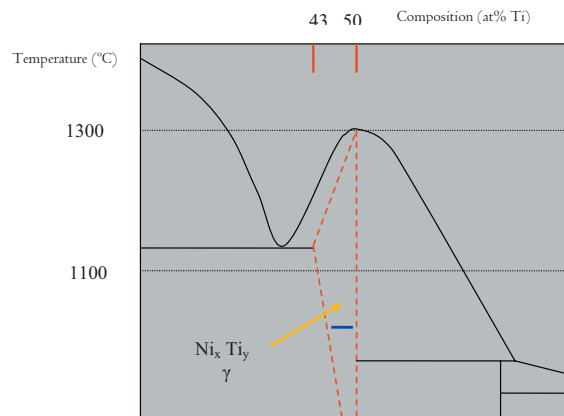
Unloading follows almost the same way. Region labelled as E-F is the martensitic way back to the austenitic phase that will be recovered at G after a gradual transformation. It is worthwhile noting that F-G region is clinically very important. It represents the pseudoelastic region in which the before mentioned superelastic effect is seen. This second plateau region represents the reversible transformation of martensite to austenite. Shape is changing (to an initial state) keeping force constant and this is done by a phase transformation. Providing that the archwire has been loaded in the plateau region, the pseudoelastic behaviour will be present.

There are several alloys at the orthodontics market that display a pseudoelastic effect. Although it is difficult to get technical information directly from the manufacturers, some of the archwires properties have been released publicly or have been found by clinical and basic research.

For example, Ormco's 27°C Superelastic Copper Ni-Ti™ contains additions of nominally 5 to 6% copper and 0,2 to 0,5% chromium. According to the manufacturer this product is an austenitic active wire. The addition of Copper increases its strength and gives an energy loss as measured at the plateau region. The problem with copper addition is that there is a shift in the temperature transformation temperature moving it above the ambient oral cavity temperature. The compensation of this unwanted effect is done by the 0,5% chromium addition to restore the transformation temperature back to 27°C<sup>115</sup>.

The family of Ormco's CuNiTi archwires is completed with the 35° C and 40° C Superelastic Copper Ni-Ti™. These latter two archwires have higher transformation temperatures so they will be more sensible to temperature changes in which the thermoelastic effect is especially sought.

These kinds of archwires represent what Andreasen was initially looking for but did not get at the start.



Graph 8

Graph 8, which has been in part adapted from the reference<sup>116</sup>, helps to explain what the problem was when trying to get the correct formula for the alloy.

It is a simplified Ni-Ti phase diagram that highlights the  $\gamma$  phase wherein shape memory alloys could be found: it has been limited by the red lines. As it can be seen the Ti composition (at%) has to be in the range of 43 to 50% which would correspond to approximately 41 to 45 wt% of Ti.

$$x \text{ Ti } (T^\circ\text{C})\text{A} \text{ ————— } \text{B } (T+200)^\circ\text{C } x + 3\% \text{ Ti}$$

**1°C/150 ppm Ti variation**

Attention should be focused on the blue line, which has been zoomed in for didactic purposes as follows:

Being A and B different points in the graph that represent a composition change in Ti equivalent to 3%, the change in the transformation temperature at this phase could change by 200° C. At the time of Andreasen it was known that every 150 ppm variation in composition there was a shift in the transition temperature of 1°C<sup>111</sup>. It was also understood that transition temperatures from martensite to austenite had to occur in the range of the ambient oral temperature. But due to manufacturing problems, the composition of the alloy could not be so very well controlled in order to achieve the right formula.

Ormco's 35° C and 40° C Superelastic Copper Ni-Ti<sup>TM</sup> take advantage of this fine tuning that has been achieved in the manufacturing control of the archwires as does so the Sentalloy<sup>TM</sup> Light manufactured by GAC.

## 2.1.1.2.4 NiTi and CuNiTi wires of this study

These wires present a particular shape. Some archwires used in the lingual technique have a standard form, that is, they have a preformed curvature but they do not have distocanine in-sets. These in-sets are particular bendings present on the archwires for the lingual technique that are needed to account for the difference in labiolingual dimensions among anterior and posterior segments. Photos 6 and 7 show NiTi and CuNiTi archwires for upper and lower arches.



Photo 6



Photo 7

This particular shape is called mushroom due to the fact that their shape recall it. Ormco manufactures NiTi arches and CuNiTi arches for lingual orthodontics as mushroom archwires. Due to their mechanical properties, these arches are really difficult to modify by introducing additional bendings.

Both NiTi and CuNiTi are available in three different sizes for both upper and lower arches which imply a variation in the in-set sizes. NiTi arches are available in 0.016" and 0.018" while CuNiTi arches are available in 0.017"x 0.017" and 0.017"x 0.025" that somehow cover the lack of rectangular cross section wires in NiTi.

NiTi wires are indicated for initial alignment and levelling treatment stages. Given that they have a round cross section they do not deliver torque.

CuNiTi archwires are suitable for alignment, levelling and torque correction given that they do have a rectangular cross section. The correction of rotations with this arch wire needs the help of particular ligating procedures. They can remain ligated for quite long periods of time because they are resistant to permanent deformation so they still deliver force although moderate deflections had been performed in order to ligate severely misaligned or unlevelled teeth.



Both types of archwires are not indicated for space closure mechanics due to the fact that, given their mechanical properties they do not avoid the bowing effect.

Depending on the transition temperatures there are three possible CuNiTi archwires for lingual orthodontics: 27°C, 35°C and 40°C.

Part and lot numbers of archwires used are as follows

Archwire	Part number	Lot
NiTi upper arch	205-0023	05L175L
NiTi lower arch	205-0029	05L576L
CuNiTi upper arch	205-0075	05E236E
CuNiTi lower arch	205-0078	05L188L

### 2.1.1.3 Titanium Molybdenum Alloy (TMA)

#### 2.1.1.3.1 Introduction, history and properties

It is known that unalloyed titanium can exist in two allotropic crystallographic forms. The hexagonal close-packed crystal form exists at temperatures up to 1625°F. Once above this temperature titanium arranges itself in a body-centered cubic configuration. Low temperature form is conventionally designated as “alpha” form, while the high temperature form is termed as “beta.”

Molybdenum, columbium, tantalum and vanadium tend to stabilize the beta-titanium phase and cause a lowering of the alpha to beta transformation temperature because they themselves have a body-centered cubic configuration. The beta to alpha transition can be inhibited if the alloy is stabilized at the beta phase and it is rapidly cooled obtaining the desired alloy at room temperature.

Titanium that has been sufficiently alloyed with elements that act as beta-stabilizers that allow keeping the cubic structure during cooling to room temperature from the beta phase is termed beta-stabilized titanium alloy or simply beta-titanium alloy.

The main element is titanium that accounts for the 25% of weight. Additional alloying elements

besides the beta-stabilizers are manganese, iron, chromium, cobalt, nickel, copper, aluminium, tin and zirconium.

Complex orthodontic shapes like closing loops and T-loops can be formed in the wires thanks to the high ductility present in the material and its excellent plasticity provided by the bcc structure. Cold working and heat treatment give the material its high strength and deep hardenability. By heat treatment the beta phase is able to contain a precipitated alpha phase which greatly increases the strength. The beta-stable phase, either in its solution heat treated state or fully annealed is very ductile and can be given the desired shape. It can also be done after partial or complete strengthening.

According to the information contained at the patent typical beta-titanium alloys have the following approximate alloying compositions:

- A. 13% vanadium, 11% chromium, and 3% aluminium;
- B. 8% molybdenum, 8% vanadium, 2% iron and 3% aluminium;
- C. 11.5% molybdenum, 6% zirconium and 4.5% tin; and
- D. 3% aluminium, 8% vanadium, 6% chromium, 4% zirconium and 4% molybdenum.

### 2.1.1.3.2 TMA in orthodontics

In 1979, Goldberg and Burstone published the first article regarding TMA and its applications in orthodontics. So far, TMA research was focused in the aerospace materials engineering field.

TMA stands for Titanium Molybdenum Alloy or also known as beta-titanium. As it has been the case for other materials and alloys, TMA was not initially thought to be used for orthodontic purposes but some researchers from the orthodontic field saw a possible application and patented its use for orthodontics.

It was patented as the US patent n° 4,197,643 on the 15th April 1980 by Burstone and Goldberg. Most of the information that will be presented on this alloy has been directly obtained from the US Patent and Trademark Office at the [www.uspto.gov](http://www.uspto.gov) the 11<sup>th</sup> February 2007.

The fact that the patent has recently expired has given rise to a new introduction of TMA wires in the market which was so far only covered by a couple of wires. Still, there is not much information available about the alloy nor in textbooks nor in the internet.

TMA was seen to be a possible solution for the disadvantages that both stainless steel and NiTi alloys had. NiTi was seen to be very ductile but the material could not withstand cold bending into orthodontic shapes like closing loops, T-loops and so forth. This was a limitation that NiTi presented, neither it could be welded or soldered. TMA could overcome these disadvantages while keeping most of the great achievements the NiTi had, the most important of them being the delivering of a continuous light force for quite a long time.

Physical, mechanical and chemical characteristics of TMA were studied in different articles appeared during the 1980s<sup>117-133</sup>. When used in orthodontics the alloy was seen to have low stiffness, high formability, good spring-back and the possibility of being welded<sup>134</sup>. Some of the studies showed that the alloy had a clear disadvantage when compared to stainless steel and NiTi: it had a high friction coefficient.

TMA was somehow seen as the missing link between NiTi and stainless steel. Burstone understood that a stiffness progression was needed in order to achieve a progressive tooth movement. Considering only the existence of gold, stainless steel, cobalt chromium and NiTi there was a gap in terms of modulus of elasticity which was still not covered. Burstone advocated the need of a continuity of the moduli of elasticity with his 'Vari-modulus orthodontics' concept<sup>135</sup> and this was one of the factors that led him get into the research of new alloys.

In order to get an idea it should be recalled that the gold archwires fitted in the original standard edgewise appliance had an elastic modulus of 15 x 10<sup>6</sup> pounds per square inch (psi) when brackets with a 0.022" slot were used<sup>118</sup>. Austenitic stainless steels developed in the 1940s for orthodontic use had an elastic modulus around 23 x 10<sup>6</sup> psi. Although less expensive than gold, stainless steel archwires needed being downsized in order not to deliver excessive forces to teeth rendering them painful and useless for orthodontics. Cobalt chromium alloy (like Elgiloy) had an elastic modulus around 28 x 10<sup>6</sup> psi<sup>118</sup>. Although being higher than stainless steel, Elgiloy had the advantage that unlike stainless steels it could be manufactured in different tempers that allowed the introduction of preformed loops. The stoichiometric NiTi alloy introduced by Andreasen in 1978 under the name of Nitinol had an elastic modulus of 4.8 x 10<sup>6</sup> psi although initially this wire did not meet the shape memory effect properties as it was seen before<sup>136</sup>. Burstone's TMA archwire had an elastic modulus of 9.4 x 10<sup>6</sup> psi and Beta-Titanium elastic modulus fell in a range of 8-16 x 10<sup>6</sup> psi. As it can be seen both archwires helped completing the array of possible elastic modulus<sup>117</sup>.

Up until quite recently, TMA wires for orthodontics were only available from Ormco as TMA and Titanium Niobium. TMA patent expired not long ago giving as a result the introduction of new companies as manufacturers of TMA wires. A wide variety TMA archwires that can be found nowadays at the market like Beta III Titanium (Unitek), Beta CNA (Ortho Organizers), Bendaloy (Rocky Mountain), BetaTi (Highland metals), Resolve (GAC), Titanmoly (G&H Wire Company), Full Range Titanium Alloy (Lancer Orthodontics) and the initial ones presented by Ormco.

Initial TMA and Titanium Niobium archwires were manufactured in different sizes: 0.016x0.022, 0.017 x 0.025, 0.0175 x 0.0175 and 0.021 x 0.025. The new eight vendors before mentioned introduced new sizes: 0.018 x 0.018, 0.020 x 0.020 and 0.021 x 0.021. The study by Johnson<sup>133</sup> reached different conclusions among which it was stated that a wider range of stiffness choices are now available making them more suitable for working and finishing wires and it is stated that TMA can now replace stainless steel as finishing wire.

### 2.1.1.3.3 TMA archwire of this study

This wire is available from Ormco for the lingual technique in the following dimensions: 0.016, 0.0175 x 0.0175 and 0.017 x 0.025.

It delivers a moderate force when engaged so it will be quite easy to get to the slots of moderately crowded or misaligned teeth. It is a comfortable wire for the patient. Bends and loops can be formed on it so it can be used as a space closure archwire but its high friction behaviour has to be taken into account. The archwire chosen for the study has been the 0.016 which is normally used for initial levelling and aligning, it is shown in photo 8.



Photo 8

Given its mechanical properties, this archwire is not expected to correct rotations completely. It represents a very good option when NiTi archwires can not be engaged due to the fact that their pre-formed mushroom shape with in-sets already present at the wire can not fit the shape of the arch in part due to the inter-canine distance.

Given its resistance to permanent deformation it can stay in mouth for long periods of time when compared to other archwires.

Part and lot numbers of archwires used are as follows:

Archwire	Part number	Lot
TMA 0.016	202-0025	05J37J

#### 2.1.1.4 Compositions of archwires

In order to get a good analysis of the data obtained from the corrosion studies and the Ni leaching test, it is necessary to know the exact composition of the archwires. Given that different authors and research teams have undergone this work, their findings will be presented and our analysis will be based on their findings.

Taking into account that there has not been any published study on lingual orthodontics archwires leaching, the weights of the archwires have been found in order to establish the amount of the elements present in the archwires following the composition in % found in the studies previously stated.

##### Stainless Steel

Ormco uses AISI type 304 Stainless Steel for its stainless steel archwires which in our study are the Respond, D-Rect, SS 0.016, and SS 0.016x0.022.

The composition as recently determined by some authors<sup>32</sup> is the following:

18% Cr, 8% Ni, 2% Mn, 1% Si, 0.08% C

## Nickel-Titanium

Some authors that have used Ormco's 0.016 NiTi archwires for their research purposes found the following compositions:

55% Ni and 45% Ti <sup>24</sup>

57% Ni and 43% Ti <sup>70</sup>

Other studies that used different Ormco cross-section archwires found the following

0.016x0.022 (atomic percentage)

52.4% Ni and 47.6% Ti <sup>137</sup>

51.3% Ni and 48.7% Ti <sup>137</sup>

Unknown cross-section

55% Ni and 45% Ti <sup>10,29</sup>

55.5% Ni and 44.1% Ti <sup>31</sup>

## Copper-Nickel-Titanium

Different authors have obtained the following compositions for CuNiTi Ormco's archwires although cross-sections were not specified.

50.7% Ni, 42.4% Ti, 6.9% Cu <sup>138</sup>

48% Ni, 46.5% Ti, 5.5% Cu <sup>10,29</sup> (Ormodent)

## Titanium Molybdenum Alloy (TMA)

Many references exist on the composition of this archwire

78% Ti, 11% Mo, 6% Zr, 4.5% Sn <sup>13,14</sup> (0.016x0.022)

78% Ti, 11.5% Mo, 6% Zr, 4.5% Sn <sup>24</sup> (0.016)

78% Ti, 11% Mo, 6% Zr, 4% Sn <sup>137</sup> (0.016x0.022)

77.8% Ti, 11.3% Mo, 6.6% Zn, 4.3% Sn <sup>31</sup> unknown cross-section

77.8% Ti, 11.3% Mo, 6.6% Zn, 4.3% Sn <sup>11,12</sup> (0.018)

75.5% Ti, 14% Mo, 5.5% Zr, 5.5% Sn <sup>10</sup> unknown cross-section (ormodent)

75.10% Ti, 13% Mo, 7.2% Zr, 4.7% Sn <sup>17</sup> (0.016x0.022)

A study<sup>7</sup> has been discarded although it presented archwires compositions that would be useful for our study. The reason is that the values seem to have been miswritten, switching Ni and Ti values as they state:

Ni-Ti: 54% Ti, 45% Ni, less than 1% other. Lot number 01B230B.

Co-Ni-Ti: 49% Ti, 45% Ni, 5% Cu, less than 1% other. Lot number 02J234J

The examined wires were also from Ormco.

For our research purposes the following composition percentages have been taken as references:

SS: 8% Ni

Ni-Ti: 55% Ni

Cu-Ni-Ti: 50% Ni

TMA: no nickel present

## 2.1.2 The electrolyte

The experimental setting of the electrochemical study follows the requirements established by the International Standards Organization. The biological evaluation of medical devices is regulated by the following norm:

Biological evaluation of medical devices. Part 15: Identification and quantification of degradation products from metals and alloys (ISO 10993-15:2000)

According to the norm, the electrolyte to be used has to be properly specified as a product for the given purpose. It has to fulfil the analytical purity and it has to be dissolved in class 2 water according to the ISO norm 3696. The first option to be used according to the norm is an aqueous solution of sodium chloride at 0.9%. Other electrolytes like artificial saliva and artificial plasma can also be used.

All the electrochemical assays were done using the Hank's Balanced Salt Solution (HBSS) as the electrolyte manufactured by Sigma®. It is a saline fluid that simulates the ionic physiological environment.

The formulation provided by the manufacturer at [www.sigmaaldrich.com/catalog/search](http://www.sigmaaldrich.com/catalog/search) (H6648) in August 2006 was as follows:

CaCl<sub>2</sub>•2H<sub>2</sub>O  
MgSO<sub>4</sub>  
KCl  
KH<sub>2</sub>PO<sub>4</sub>  
NaHCO<sub>3</sub>  
NaCl  
Na<sub>2</sub>HPO<sub>4</sub>  
D-Glucose  
Phenol Red•Na

At table 3 the amount of ions can be seen for the used solution.

	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>	pH
HBBS	141,7	5,8	0,9	1,3	147,7	4,2	0,78	7,2
Human plasma	142	5	1,5	2,5	103	27	1	variable

Table 3

Some corrosion studies have been done using the Fusayama-Meyer preparation or even some modifications of these preparations which essentially contain the following:

KCl  
NaCl  
CaCl<sub>2</sub>•2H<sub>2</sub>O  
NaH<sub>2</sub>PO<sub>4</sub>•2H<sub>2</sub>O  
Na<sub>2</sub>S•9H<sub>2</sub>O  
Urea  
KSCN (modified Fusayama Meyer)



These preparations have been used widely in this kind of experimentation and references can be found in different articles<sup>15,139,140,141</sup>.

The electrolyte was renewed for each experiment when corrosion testing was performed at the potentiostat. A bottle of 500ml was used for three to four tests of different archwires (photo 9)



Photo 9

### 2.1.3 The reference electrode

The reference electrode that has been used for the electrochemical experimentation is an Ag/AgCl/KCl electrode that can not be polarized and it has a  $E^{\circ} = 0.222 \text{ V}$ . During the assay the potential difference between the working electrode and the auxiliary electrode is controlled. This potential difference is measured thanks to the reference electrode.

This electrode does not take part in the circuit. There is no current across it. It only serves as a reference in order to test the working electrode.

Potential drops that might occur in the solution due to its own resistance, like an IR drop, could be added to the measured potential. In order to minimise this risk, the reference electrode is kept in contact with a solution through a tube that ends in a thin capillary tube known as Luggin (photo 10)



Photo 10

## 2.1.4 The auxiliary electrode

The auxiliary electrode (Radiometer Analytical, Villeurbanne, France) used in the experimentation is made of platinum and it has a surface of 240 mm<sup>2</sup>. This electrode is necessary in order to close the circuit and has to be inert to the tested electrolyte. That is why platinum and graphite are normally used as auxiliary electrodes (photo 11)



Photo 11

## 2.1.5 The potentiostat

A potentiostat is an electronic device that allows changing the potential of the working electrode in a controlled manner. Then, measures of current flows can be obtained as a function of the applied potential (photo 12)



Photo 12

There are two kinds of measurements that can be done with the potentiostat. Potentiostatic measurements are characterized by the fact that potential is all the time controlled, while galvanostatic measurements are those in which the current is controlled. In both cases, may one measurement be done or the other, the working electrode is said to being polarized.

Potentiostatic methods are more common than galvanostatic methods.

All metals have an equilibrium potential, which is the potential value that a metal takes in absence of electrical connections. It is most times referred as the Open Circuit Potential (OCP). The first step in most electrochemical experiments is to obtain the OCP because it is characteristic of every metal and it is normally set as the zero value in potentiostatic measurements.

When the OCP of a metal is known, the electrochemical set up of the working electrode, the auxiliary electrode and a reference electrode connected to a potentiostat allow performing corrosion measurements that will help understand the resistance of a material in a certain environment and lead to establish conclusions comparing different metals.

Thanks to the potentiostat, once the OCP of a metal is known, the potential of a metal can be forced away from this value and the metal will be in process of being polarized.

When the potential is forced away from OCP to more positive potentials in relation to this value, the metal is being moved towards the anodic region. Being in the anodic region of a material means that its behaviour can be stated to be corrosive. When the metal, by the applied potential, is anodic, cathodic reaction is not being balanced because the potentiostat does not allow it to be so. Then a net current flows from the electronic circuit into the metal sample.

The electrochemical testing has been performed on an electrolytic cell where the three electrodes were in contact with the electrolyte across three holes that isolated the electrodes and the electrolyte from the outer environment (photo 13).



Photo 13

In the case of the working electrode, a silicon plug was used so the wire could be fitted and be fixed into the hole that was at the socket of the electrolytic cell. The electrolytic cell was

submerged on a bath of water that by means of a thermostat kept the working temperature of the electrolyte at 37°C (photo 14).

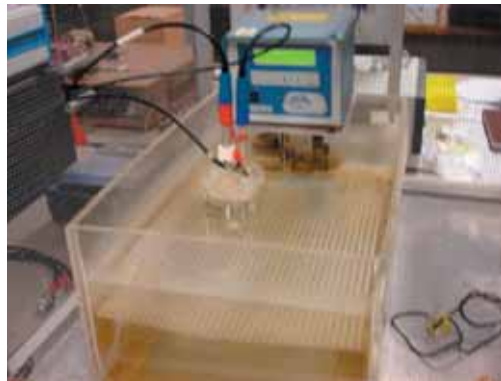


Photo 14

This setting was surrounded by a metal case that protected the assay from being touched or moved by other laboratory technicians. It was plugged through the electrodes to the potentiostat, a VOLTALAB PGZ 301, which at the same time was connected to a computer that controlled the system through a software package called VOLTAMASTER4 (photo 15)

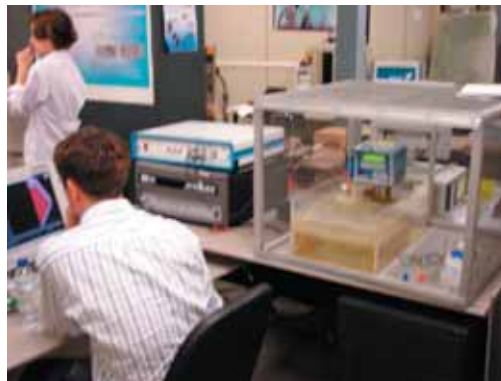


Photo 15

This material belongs to the Biomaterials Laboratory based at Escola Tècnica Superior d'Enginyeria Industrial de Barcelona at the Universitat Politècnica de Catalunya.

## 2.2 The methods

### 2.2.1 Preparation of specimens

#### 2.2.1.1 Specimens for corrosion testing at the potentiostat

Initially, three segments of each wire were cut in order to be able to test the same arch three times in order to obtain reproducible results and see the initial variability among specimens of the same material. The specimens were cut in such a way that a length of 2.5 cm was immersed in the electrolyte for corrosion testing. At the point where the specimen reached the electrolyte interface, a bee wax round pad was put in order to obtain measurements that were not biased by the change that the interface introduced (photo 16)



Photo 16

After being prepared, the specimens were ultrasonically cleaned for 4 minutes on a conventional ultrasonic bath (photo 17) using deionized water and rinsed with acetone for degreasing previous to the electrochemical assay (photo 18)



Photo 17



Photo 18

### 2.2.1.2 Specimens for Ni ionic release testing

Ni ionic release testing was designed in such a way that two archwires were analyzed for ionic leaching simulating the amount of Ni that would be released when both arches are engaged in mouth.

Segmented archwires were introduced in six plastic vials (photo 19) and were submerged with 4 ml of HBBS and 0.1 ml of HNO<sub>3</sub> at 65% (PANREAC®).



Photo 19

The addition of the acid was done in order to avoid that, given the vertical position of the vials and archwires segments, once the 4 ml HBBS was extracted to be analysed, there were Ni ions remaining at the bottom of the vials and analyzed results were not accurate.

The vials were kept at a heating temperature of 37°C (see photo 20) and liquid extractions of the full amount of HBBS were performed at 7 days, 14 days and 30 days. The vials were refilled as explained three times for the three analysis and the Ni release final values result of the cumulative addition of the results. An empty vial was also tested as a control to see how much Ni could be detected.



Photo 20

### 2.2.1.3 Specimens for macroscopic photography, SEM and AFM analysis

Once corrosion and immersion testing for Ni release were performed, specimens were prepared for image studies through macroscopic photography, SEM and AFM.

Macroscopic photography was done on specimens that had been tested at the potentiostat and as-received specimens.

SEM was done on specimens that had been tested at the potentiostat, immersed specimens for 30 days and as-received specimens. Four fragments of 3 mm of each archwire were placed on a conventional SEM holder after being cleaned ultrasonically, degreased and dried with deionized water, acetone and alcohol. AFM specimens followed a similar preparation protocol (see photo 21)

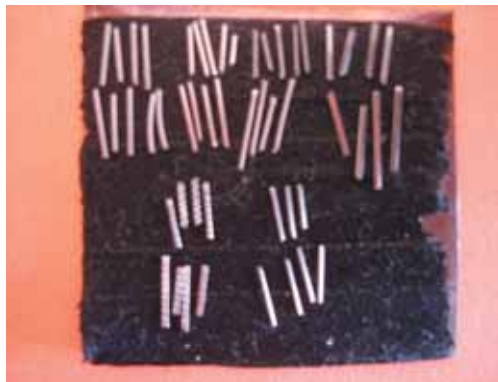


Photo 21

### 2.2.1.4 Specimens for calorimetry

NiTi and CuNiTi archwires were prepared for calorimetry testing. Tiny cuts of the archwires were prepared about 2 mm long. Specimens were prepared from as-received archwires, archwires that had been submerged for 30 days and archwires that had been tested on the potentiostat. They were cleaned with the previously stated protocols for corrosion testing, Ni ionic release testing and image analysis.

## 2.2.2 Open circuit potential (equilibrium potential, rest potential)

It is the first measurement of the corrosion test. As it has been said, it is necessary to know the OCP value of the specimen in order to know where its corrosion starting point is located in relation to other materials and because it will be set as the initial zero value for the following measurement, the cyclic voltammetry.

When determining the OCP, the working electrode is acting as a battery, establishing the generated potential between the auxiliary electrode and the working electrode. This measurement has been performed for three hours which is normally enough time to get a stable measurement. The VOLTALAB was set in order to take up records every two seconds. The ISO 10993-15 sets a minimum time of two hours for the test. OCP is a difficult value to obtain and stabilise due to the fact that any problem with connections could alter the readings of the potentiostat. The higher the value at which the material gets its stabilization potential the more resistant to corrosion the material will be.

At this potential there is no current present that can be measured, current equals zero.

Given that it is a difficult parameter to stabilise different measurements were taken.

When the VOLTALAB finishes the OCP measurement of the specimen, the cyclic voltammetry test will automatically start because the computer has been set in order to do it in such a way, starting from the obtained OCP value.

## 2.2.3 Cyclic Voltammetry

It is a test by which the potential is changed as a linear function of time, based on the linear potential waveform. The rate of change of potential with time is referred to as the scan rate.

This test is very useful to see at which potential the current density is no more zero at takes up a value that indicates current flow starts to exist.

The potentiostat was programmed in order to do the following measurement with the specimens.



The initial potential was set to be the free potential, that is, the potential obtained at the OCP. The open circuit potential, also known as rest potential is most times labelled as  $E_r$ .

$E_r$  establishes a limit where potentials below it are always protecting potentials, that is, the specimen will be protected against corrosion as long as the potentials to which the specimen are subjected are kept under this value. Above  $E_r$  the potentials cause the specimen to corrode freely in the electrolyte. Therefore general corrosion on a specimen starts around the  $E_r$  value. The transition of the specimen from being cathodic to anodic is always centered around the  $E_r$  and when a current starts to be measured around this point, general corrosion is said to start.

Cyclic Voltammetry establishes the  $E_{corr}$ . This is the potential at which current starts flowing and it determines the exact point around the OCP where pitting corrosion starts. It is sometimes referred as pitting potential, corrosion potential or breakdown potential. The current measured at  $E_{corr}$  is known as  $i_{corr}$  and it can also be used to obtain the instantaneous corrosion rate (ICR) sometimes measured in mm/year of loss of material.

Afterwards, two limits were set for the potential: an upper limit and a lower limit. The lower limit was normally set at -300 mV and the upper limit at +2000 mV measured from the OCP, that is, for a given OCP, a scan was done 300 mV under that value (cathodic region) and 2000 mV above the OCP value (anodic region). The scanning rate was set at 0,25 mV/sec. The test took around 8 hours to be completed and only 1 cycle per specimen was performed meaning one backward and forward scan. The minimum current to be allowed was set at -1 A, the maximum at +1A and the minimum range of current at 100 $\mu$ A.

This is in agreement with the ISO 10993-15 norm for this kind of tests.

Some modifications at the upper limit of potential had to be done in order to obtain some corrosive destruction given that +2000mV was not enough for the TMA archwires and had to be set at +2700mV.

Results of OCP and CV were saved in EXCEL sheets in order to analyse the results and obtain the graphs of the measurements.

## 2.2.4 Image study

### 2.2.4.1 Photographs

Macroscopic photographs were taken in order to get images of as-received specimens and images of corrosion of the specimens tested at the potentiostat. Images from the 30 day immersed specimens were not taken because there was not a macroscopic difference that could be certified.

Photographs were taken with an OLYMPUS CAMEDIA C5060 WIDE ZOOM digital compact camera coupled to an OLYMPUS SZ 51 Microscope with a KL 1500 LCD light filter (see photo 22)



Photo 22

This material belongs to the Biomaterials Laboratory based at Escola Tècnica Superior d'Enginyeria Industrial de Barcelona at the Universitat Politècnica de Catalunya.

### 2.2.4.2 Scanning Electron Microscopy

The SEM analysis was done through images taken with a JEOL JSM-6400 electronic microscope with an EDS (Energy Dispersive Spectroscopy) Link Analytical LZ-5 detector. Images could be edited and treated with INCA Mapping software. This microscope is based at the Escola Tècnica Superior d'Enginyeria Industrial de Barcelona at the Universitat Politècnica de Catalunya (see photo 23)



Photo 23

### 2.2.4.3 Atomic Force Microscopy

This image technique allows very detailed analysis of material surfaces and it can display the results in three dimension graphs. It is a non-destructive microscope technique that belongs to a group of microscopes that gathers together different scanning probe microscopes.

Surface analysis is performed without a direct contact with the specimen. Very small areas can be examined that range from atomic level to  $125 \mu\text{m}^2$ . Specimens do not need a special preparation previous to the analysis and this makes this technique quite time saving and fast.

The specimen is fixed to a scanning piezo that has three degrees of freedom for translational displacement. The surface of the specimen is scanned with a very fine tip that is mounted on a cantilever. The tip typically has a curvature radius around 20 to 40 nm with a length of  $200 \mu\text{m}$  and a thickness of  $0.5 \mu\text{m}$ . The tip gets to a distance to the surface around 100 nm at which coulombian forces cause the tip to bend. This vertical deflection is transmitted to a cantilever which is holding the probing tip. The cantilever has a laser beam at his posterior side which captures the cantilever deflection. A segmented photodiode is the responsible of registering the variations of the cantilever that are translated into shifts of the light spot out of the centre of the capturing photodiode.

The piezo-driven platform uses the information being recorded by the probing in order to keep a constant vertical distance between the tip and the specimen's surface so contact is avoided. Scans are performed in different lines in order to obtain a full topography of the surface which can be finally displayed in a three dimensional graph (see figure 8)

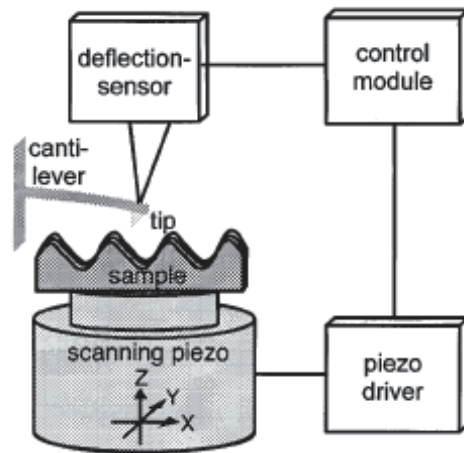


Figure 8

The following websites present a full description of the AFM technique and they can be used in order to get a full knowledge of the technique:

<http://stm2.nrl.navy.mil/how-afm//how-afm.html#standard%20modes>

[www.afmuniversity.org](http://www.afmuniversity.org)

This technique is very useful to determine surface topography of specimens and surface roughness. It has been decided to use it to get a comparison between as-received archwires and archwires immersed for 30 days to study whether surface differences do really exist. Comparing SEM images of both groups is sometimes difficult and surface changes are difficult to be detected in an objective way that is, not being biased by the fact that it is known that one of the groups had been exposed to the electrolyte.

The study was performed on a Pacific Instruments Atomic Force Microscope (Pacific Nanotechnology, Santa Clara, CA) at the scientific support services of the University of Barcelona.

The chosen sections for the AFM study of the archwires were  $20\ \mu\text{m} \times 20\ \mu\text{m}$ . The wires chosen for the study were all but the TMA wire which was not tested for Ni release.

AFM image study was performed with the scanning probe microscopy software WSxM 4.0 Develop 10.4 developed by Nanotec Electronica SL (2007)<sup>142</sup>.

For each specimen, ten randomly chosen sections of 2  $\mu\text{m}$  x 2  $\mu\text{m}$  were zoomed and RMS was measured for them in order to perform the t-student test for the significance of the means and hence finding whether the RMS shows changes in the surface of the archwires.

The as-received and immersed specimen were cut from the very same archwire so comparisons could be established and statistical t-student analysis could be performed reducing the inter archwire variability.

It is assumed that the mean of a sample randomly drawn from a population that follows a normalized distribution it also follows a normal distribution of its normal means, hence, the mean of the distribution under sampling needs being identical to the population mean, being  $\mu_M = \mu_{\text{source}}$ . Therefore for two samples randomly drawn, the difference between the means  $M_a - M_b$  belongs to a normal distribution where the overall mean is equal to the difference of the means of the two populations under consideration, therefore  $\mu_{M-M} = \mu_{\text{source A}} - \mu_{\text{source B}}$ .

On the null hypothesis, in the case of the present research is that there is no RMS change due to the immersion of the archwires in HBSS for one month.

Therefore it should follow that  $\mu_{\text{source A}} = \mu_{\text{source B}}$  and therefore  $\mu_{M-M} = 0$ .

Given that as in most studies occur, the variance of the source population for the RMS is unknown, the variance has to be estimated and this is why in such studies the test for the null hypothesis has to be tested with a t-test instead of a normalized z.

In general:

$$\sigma_{M-M} = \sqrt{(\sigma^2/N_a + \sigma^2/N_b)}$$

where the null hypothesis could be tested for any chosen  $M_a - M_b$  difference by setting the right z ratio at:

$$z = \frac{M_{x_a} - M_{x_b}}{\sigma_{M-M}}$$

Given the need of using a t-test, therefore

$$t = \frac{M_{x_a} - M_{x_b}}{\text{estimated } \sigma_{M-M}}$$

which it will be labelled as  $t_{obs}$  as the observed value in the present research where the result value belongs to a particular sampling distribution of  $t$  defined by its degrees of freedom

$$df = (N_a - 1) + (N_b - 1)$$

**estimated  $\sigma_{M-M}$**

$$\text{estimated } \sigma_{M-M} = \sqrt{[ \{s_p^2\}/N_a + \{s_p^2\}/N_b ]}$$

$$\text{being } \{s_p^2\} = (SS_a + SS_b) / (N_a - 1) + (N_b - 1)$$

where  $SS$  stands for the sum square of the differences of the RMS values to the found mean.

The  $df$  for the present study is 18. Therefore, the  $t$  values with respect to which the  $t_{obs}$  will be compared as shown in the  $t$  values from the distribution table are as follows:

One-tail values	Level of significance for a non-directional test						
	0,1	0,05	0,025	0,01	0,005	0,0025	0,001
t for $df=18$	1,33	1,734	2,101	2,552	2,878	3,197	3,61

## 2.2.5 Nickel leaching

The analysis of Ni release has been performed through Atomic Absorption Spectrometry (AAS) in a graphite furnace.

The test was done on 4 ml of electrolyte that had been in contact with the archwires for 7, 14 and 30 days and a blank test that was done on a 4 ml vial that was not in contact with any archwire in order to establish a control measurement.

TMA archwires were not tested for Ni release given that they do not contain this element.

Six vials were prepared with the following content:

- Vial 1 (Respond): 2 archwires
- Vial 2 (D-Rect): 2 archwires
- Vial 3 (ss 0.016x0.022): 2 archwires
- Vial 4 (ss 0.016): 2 archwires
- Vial 5 (NiTi): 4 archwires
- Vial 6 (CuNiTi): 4 archwires
- Vial 7 (empty): control with no content

The AAS in graphite furnace is an elemental analysis technique based on the study of the absorption of the atomized particles of the examined material through heating. In the case of the present technique the source of heat is electrical so a higher atomization performance is achieved.

During the test, the liquid to be analysed is introduced in the graphite furnace where it is evaporated and atomized. Then a radiation source is applied called hollow cathode lamp that is only prepared to analyse one element, which is the one of what the cathode lamp is made of (see figure 9)

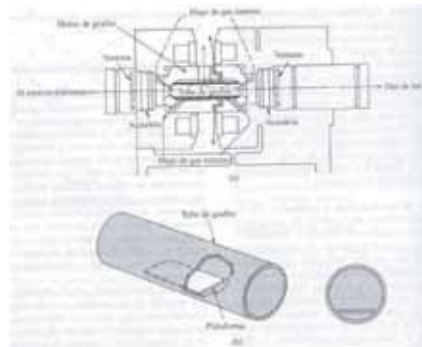


Figure 9

This technique has the lowest detection limits possible. It even gets lower detection levels than the Plasma ICP Atomic Emission Spectroscopy. This latter has the advantage of being able to undertake a multielemental analysis at one time so the testing time is shorter in the case of studying more than one element. The lowest limit for Ni detection at the AAS in graphite furnace with electrothermal source is 0.61 ppb (ng/l).

## 2.2.6 Calorimetric analysis

As found at the internet<sup>76</sup>, “differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of

a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions.”

This test was performed on NiTi and CuNiTi archwires to see what phase transformation temperatures do the lingual archwires have and how the 30 day immersion and the potentiostatic anodic polarization modified those parameters.

The transformation behaviour and phase transition temperatures have been determined by a thermal analysis called differential scanning calorimetry (DSC) in the temperature range from -90°C to 200°C with a 2920 Modulated DSC V2.4F instrument (TA Instruments, New Castle, DE) (see photo 24)



Photo 24

The calorimetric analysis was done on three samples for each archwire: an as-received sample, a 30 days immersed sample and a polarized sample. All of them were tested for two cycles in order to obtain more accurate results, although results displayed are those obtained for the second cycle.



Some difficulties arose when trying to gather enough material for the polarized samples due to the fact that after the polarization test at the potentiostat, most archwires were really corroded and there was a high loss of structure. But in the end enough material could be used for the DSC.