AN IN VITRO INVESTIGATION OF THE EFFECTS OF SURFACE CORROSION ON THE METAL ELEMENT CONTENT AND TENSILE STRENGTH OF ORTHODONTIC SILVER BRAZED STAINLESS STEEL JOINTS ARISING FROM VARYING EXPOSURE PERIODS IN FUSAYAMA'S ARTIFICIAL SALIVA

by

ANISA VAHED

____________________ 09/12/2004

APPROVED FOR FINAL SUBMISSION

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Mr G.B. Somers **Date**
M.Deg. Dental Tech. *(Cum Laude)* (TN)
Reg. Dental Tech. (S.A.D.T.C)

SUPERVISOR

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ANISA VAHED

DISSERTATION SUBMITTED IN COMPLIANCE WITH THE REQUIREMENTS FOR THE MASTER'S DEGREE IN TECHNOLOGY: DENTAL TECHNOLOGY, IN THE DEPARTMENT OF DENTAL SERVICES, DURBAN INSTITUTE OF TECHNOLOGY

I, Anisa Vahed, declare that this dissertation represents my own work, both in conception and execution.

____________________ 09/12/2004

Supervisor: Mr G.B. Somers
M.Deg. Dental Tech. *(Cum Laude)* (TN)
Reg. Dental Tech.

Co-supervisor: Prof N. Lachman
B.Med.Sc, M.Med.Sc *(Cum Laude)* (UDW)
PhD: Clinical Anatomy (UDW)

DEDICATION

This study is dedicated to the greatest power,
Through which all things are made possible, my **creator**,
ALLAH ‘TAALA *(ٱللَّٰه GOD)*

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"The path to our destination is not always a straight one. We go down the wrong road, we get lost, we turn back. Maybe it doesn't matter which road we embark on. Maybe what matters is that we embark".

Barbara Hall (1993)

With the preceding words that aptly describes my journey of many disappointments but ***"doomed not"*** the support of those holding my head high and allowing me to look the world in the face; I wish to begin this formal expression of my gratitude by acknowledging the generosity of those whose names I have been unable to recall. Indeed, the pinnacle of success is never possible through solitary effort.

"The recognition that this work may receive therefore, belongs not to the name that precedes it, but to those who have made it possible".

(Lachman, N., 2003)

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ABSTRACT

Globally in the field of Dental Technology, brazing continues to be the prevailing joining technique for removable orthodontic appliances. However, the strength of the brazed joint is a growing concern to dental technicians since the commonly employed silver solder brazing material undergoes changes in brazed joint composition (microstructure) thereby enhancing corrosion susceptibility. This ultimately influences the success of orthodontic appliances intra-orally.

The objective of this in vitro investigation was therefore to determine the effects of corrosion on the composition and tensile strength of orthodontic silver brazed stainless steel joints after varying exposure periods in Fusayama's artificial saliva.

The investigation was conducted by means of exposing four groups of 20 orthodontic silver brazed stainless steel (SBSS) joints (80 in total) to varying exposure times, consecutively at 7days, 14 days, 21 days and 28 days in Fusayama's artificial saliva. The tensile strengths of the four sprayed sample groups were measured using a tensile testing machine and their strengths were compared to the 20 orthodontic SBSS joints of the unsprayed control group (n = 100). The selection of the silver solder brazing material, at the time of survey in the study, was based primarily on its popularity in the industry, availability and cost.

Finally, the change in microstructure of the fractured orthodontic SBSS joints were then analysed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The findings of this study were documented as follows:

Contrary to the statistical evaluation used in the study, which revealed that no difference existed in the tensile strengths of orthodontic SBSS joints between the four sample groups, the mean value of the tensile strengths demonstrated that a conspicuous difference existed per exposure period.

In addition, stainless steel wires and silver solders are galvanically incompatible and when brazed together the tendency towards corrosion is potentiated. SEM/EDS analysis revealed that the composition of the orthodontic SBSS joints contained four distinct phases and that the transpiration of smooth dendritic/lamellar and star/clover patterns was characteristic of the four phases.

However, when the orthodontic SBSS joints were exposed to Fusayama's artificial saliva some of the pattern characteristics radically transformed into concave star/clover patterns. This significantly supported the increased propensity towards corrosion. Of greater importance was the fact that with prolonged exposure the patterns continued to proliferate and become more defined. This was clearly indicative of the correlation that existed between exposure period, corrosion, change in microstructure of the orthodontic SBSS joints and their combined effects thereof, which positively influenced the overall tensile strength of the brazed joints.

On a clinically universal level, this study helped to elucidate the association between exposure period, corrosion and change in composition of orthodontic silver brazed stainless steel joints and their combined effects thereof on the overall strength of the brazed joints. This study also presents an original method for simulating normal salivary conditions by introducing the in vitro machine that can be used and modified accordingly for future research. The value of this study is therefore in its data and findings, which is envisaged to create potential technical and clinical awareness.

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CHAPTER ONE

The grand aim of all science is to cover the greatest number of empirical fact by logical deduction from the smallest number of hypotheses or axioms

Albert Einstein (1879 – 1955).

THE PROBLEM AND ITS SETTING

1.1 INTRODUCTION

The clinical performance and success of an orthodontic appliance with brazed joints is dependent upon the mechanical properties of the brazed combination and its resistance to the varying environmental conditions within the mouth. The strength of silver brazed stainless steel joints (SBSS) is often reduced due to corrosion (products) resulting from the galvanic action between the parent metal (austenstitic stainless steel) and the filler metal (silver solder), as well as changes in microstructure due to heating.

In orthodontics, silver solder is commonly employed for producing silver brazed stainless steel joints in removable appliances such as the Hawley appliance. However weaknesses of the stainless steel joints are observed after placement of the appliance in the mouth. For this reason a study was necessary to determine the tensile strengths of silver solder, as it will help provide valuable data to the dental manufacturers of silver solder in terms of improving the metal element (ions) content composition and physical design of silver solders.

It is further noted that damage caused by corrosion of an appliance containing a brazed junction present both visual and microscopic observable surface changes. Past tensile strength and corrosion studies on brazed joints have simply immersed and observed the surface of the alloy before and after exposure to a corrosive environment. Very little attempts have been made to expose them to a physiological saline medium simulating the oral environment. This lack of data in the relevant literature further necessitated an in vitro approach to be used that simulated normal salivary conditions. Although many investigators question the reliability of an in vitro approach, this method was nonetheless used for this study in an attempt to provide further data into the effects of surface corrosion on the strength and microstructure of the sample groups, as it will serve to have application for future in vivo studies.

1.2 THE PROBLEM AND ITS SETTING

1.2.1 THE STATEMENT OF THE PROBLEM

The purpose of this *in vitro* examination is to determine the effects of surface corrosion on the metal element (ions) content and tensile strength of orthodontic silver brazed stainless steel joints arising from varying exposure periods in Fusayama's artificial saliva.

1.2.2 SUBPROBLEMS

1.2.2.1 SUBPROBLEM ONE

The first subproblem is to determine the tensile strength of orthodontic silver brazed stainless steel joints using a tensile testing machine in order to identify parameters for comparison with the control and to further ascertain whether the fracture occurred in the solder, the parent metal or the interface.

1.2.2.2 SUBPROBLEM TWO

The second subproblem is to determine the extent of the surface corrosion and the metal element (ions) content of the fracture using a scanning electron metallographic microscope and an energy dispersive X-ray analysis system for the purposes of identifying microstructural changes in comparison to the control.

1.2.2.3 SUBPROBLEM THREE

The third subproblem is to determine the relationship between the exposure periods and microstructure of orthodontic silver brazed stainless steel joints in order to establish their combined effects on the tensile strength of orthodontic silver brazed stainless steel joints.

1.2.3 THE HYPOTHESES

1.2.3.1 HYPOTHESIS ONE

It is hypothesised that the orthodontic silver brazed stainless steel joints will produce different levels of predictability and tensile strengths to the control, and will thereby set parameters for comparison.

1.2.3.2 HYPOTHESIS TWO

It is hypothesised that the orthodontic silver brazed stainless steel joints will produce different levels of predictability and differences in microstructure to the control, and will thereby set parameters for comparison.

1.2.3.3 HYPOTHESIS THREE

It is hypothesised that a relationship between the exposure periods and microstructure of orthodontic silver brazed stainless steel joints exists and their combined effects influences the change in the tensile strengths of orthodontic silver brazed stainless steel joints

1.2.4 ASSUMPTIONS

1. It was assumed that the flux recommended by the silver solder manufacturer will help facilitate adequate wetting of the recommended solder and that there would be no flux inclusion at the brazed joint and hence not affect the strength of the brazed joints.

2. It was assumed that the austenitic stainless steel orthodontic wire and silver solder were flawless.

3. According to Leung and Darvell (1997) the use of a physiological saline simulating normal salivary conditions produces results that closely approximate natural saliva. Consequently, it was assumed that Fusayama's artificial saliva used for this in vitro study would simulate normal salivary conditions and will thus not greatly influence the extent of corrosion.

4. The economical use of an ultra violet light was assumed to be suitable and reliable to minimise the effects of bacteria on the brazed specimens.

5. The in vitro machine manufactured specifically for this study to simulate normal salivary conditions was assumed to:
    - be a product of a highly precision engineering
    - provide and maintain a regulated flow of saliva for the duration of the experimental phase.

6. Flame soldering, compared with electric soldering, resulted in joints with significantly higher tensile strength (Gawlik et al., 1996). This economical technique was assumed to produce brazed joints of superior quality.

7. It was assumed that orthodontic silver brazed stainless steel specimens experiencing greater corrosion activity would produce weaker tensile strengths.

8. It was assumed that the extent of corrosion increased with longer exposure periods in Fusayama's artificial saliva and this influences the tensile strength, metal element content and surface morphology (microstructure/composition) of the orthodontic silver brazed stainless steel joints.

1.2.5 DELIMITATIONS

1. This study will not examine the influence of the effects on:

    - varying pH levels
    - compositional changes of Fusayama's artificial saliva
    - temperatures
    - bacterial influences
    - carboxygen flow rates, and
    - the influence of any other oral environmental factors that may change the make up of the Fusayama's artificial saliva.

    However, temperature and pH levels in the test machine was monitored and recorded daily throughout the course of the study. The reason for this delimitation was to focus on the variables noted in the problem statement and to stay within the parameters of the budget.

2. Although the findings of the study will have application, this study will not evaluate the:
    - Different brazing techniques.
    - Applicability of the method of brazing.

- Gap distances of the wires to be joined.
- Allergic, cytotoxic and antibacterial effects of the brazed joints.

3. The study is aimed at testing only the tensile strengths of the brazed joint and not any other types of stresses such as fatigue stresses.

4. The study does not aim to focus on the effects of cold working and/or any other factors that may affect the tensile strength while the brazed joint is being worked off.

5. There are many different brands of orthodontics wires and silver solders available on the South African market. However, this study will be limited to the use of one brand of orthodontic wire, orthodontic solder and solder flux. Dentaurum, (Pforzheim, Germany) produces this brand. The main reason for its popularity is its cost effectiveness, speed of production (not technique sensitive) and ease of availability.

6. This study does not aim to provide potentiostat or ammeter measurements on the galvanic corrosion rates. However, a voltmeter was used to merely monitor the galvanic current rate.

1.2.6 DEFINITIONS OF TERMS AND CLARIFICATION OF CONCEPTS

1.2.6.1 SOLDERING

Soldering refers to the process whereby the fusion of metals results in an intermediary alloy, which has a lower melting point (Combe, 1992: 204) and brazing is an industrial term used to describe a soldering operation at temperatures above 500°C. Therefore for the purposes of this study, the terms soldering and brazing are interchangeable as they have the same connotation.

1.2.6.2 SOLDERING FLUX

Soldering flux is a material used to prevent the formation of, or to dissolve and facilitate removal of, oxides and other undesirable substances that may reduce the quality or strength of the soldered metal structure (Anusavice, 1996: 620).

1.2.6.3 TENSILE STRENGTH

Tensile strength is the maximal strength required for fracturing a structure and this is largely dependant upon the tensile stress that is the stress caused by a load that tends to stretch or elongate the structure (Phillips, 1991: 291).

1.2.6.4 TARNISH

Tarnish is a surface discoloration on a metal or even a slight loss or alteration of the surface finish or lustre. Tarnish is often the forerunner of corrosion (Phillips, 1991: 291).

1.2.6.5 CORROSION

Corrosion in the specific sense is not merely a surface deposit but is an actual deterioration of a metal by reaction with its environment (Phillips, 1991: 292).

1.2.6.6 PITTING CORROSION

This type of corrosion develops in localized areas, resulting in cavities or pits that can range from deep penetration of relatively small diameters to larger diameter shallow cavities (Schweitzer, 1987: 14).

1.2.6.7 BREAKDOWN POTENTIAL (BP)

The breakdown potential indicates the point at which the oxide film of the alloy is broken down and dissolution of the alloy begins (Kim & Johnson, 1999)

1.2.6.8 GALVANIC CORROSION

This type of corrosion occurs when two or more dissimilar metals are in contact, or when metals having the same analysis have different surface conditions and an electrolyte is present (Schweitzer, 1987: 16).

1.2.6.9 PASSIVITY

When a metal is capable of forming an oxide layer that is stable in the presence of an electrolyte and protects them from further corrosion, such a metal is rendered passive (Phillips, 1991: 299).

1.2.6.10 QUENCHING

When a metal is rapidly cooled from an elevated temperature to room temperature or below (Anusavice, 1996: 341).

1.2.6.11 MUCIN

Mucins are the principal organic constituents of mucus, the slimy visco-elastic material that coats all mucosal surfaces (Tabak et al., 1982).

1.2.6.12 BUFFERING

With reference to physiological saline solutions, a buffer is an ionic compound, which resists change in the concentration of an ion in solution. Buffering therefore refers to the ability of a compound to resist change in pH and in calcium ions. (Oral Environment Online, 2000-10-27)

1.2.6.13 pH

With reference to physiological saline solutions, pH is the abbreviation for potential hydrogen and for any solution it is the measure of its hydrogen-ion concentration. The higher the pH reading, the more alkaline and oxygen rich the fluid is. The lower the pH reading, the more acidic and oxygen deprived the fluid is. (Poly MVA Survivors Online, 2004-07-12)

CHAPTER TWO

Literature is strewn with the wreckage of men who have minded beyond reason the opinions of others

Virginia Woolf (1882 – 1941)

REVIEW OF RELATED LITERATURE

2.1 INTRODUCTION

The ensuing review of related literature is aimed at providing the reader first with an overview of the current position in industry with regards to orthodontic silver brazed stainless steel **(SBSS)** joints in removable orthodontic appliances. The reasons for gaining popularity are highlighted and the global concerns regarding brazed joints are raised. This aptly lends itself to a discussion of the factors influencing the microstructure of the brazed joints as this is directly related to the corrosion behaviour of SBSS joints in orthodontic appliances when placed intraorally.

The theory of corrosion then ensues with specific emphasis placed on galvanic and pitting corrosion that the brazed joints experience when placed intraorally and their effects thereof on the strength of the brazed joints. Discussion on galvanic and pitting corrosion appropriately lends itself to the discussions on the galvanic series and pit shape and growth respectively.

The review then continues to describe an overview of the different types of aqueous electrolyte systems generally advocated for in vitro studies as this directly influences corrosion susceptibility. The problem of a suitable physiological saline solution has been addressed with a brief introduction, followed by an assessment on the different types of aqueous electrolyte systems used in previous in vitro studies. This attempted to offer a logical explanation on the factors that influenced the decision on the electrolyte system used for this study.

Consequently a discussion on mucin-based artificial saliva and the carboxymethylcellulose (CMC)-based artificial saliva was facilitated and is reviewed in terms of their popularity and use by previous researchers, who have claimed that mucin-based artificial saliva have properties closely approximating those of natural saliva. Specific emphasis is therefore made on mucin-based Fusayama's artificial saliva, which has shown to produce better measurable results than the previously used Ringer's solution.

In the final analysis, the significance of the knowledge gained in this study is summarised and an explanation as to why further research on the effects of surface corrosion on the tensile strength and metal element (ions) content of orthodontic SBSS joints, are given.

2.2 OVERVIEW OF THE CURRENT POSITION IN INDUSTRY WITH REGARDS TO SBSS JOINTS IN REMOVABLE ORTHODONTIC APPLIANCES

Removable orthodontic appliances and retainers are commonly constructed from wires of stainless steel, cobalt-chromium, or a combination of both and may have one or more brazed joints holding the appliance together (von Fraunhofer, 1997). Orthodontic stainless steel wires are universally made of austenitic stainless steel containing approximately 18% chromium and 8% nickel (Barrettt et al. 1993). This metallurgical improvement facilitated greater strength, improved corrosion resistant properties and has made them amenable to brazing operations with low fusing silver solders, thereby significantly influencing its popularity and establishing its use in industry especially in the field of Dental Technology.

However, the presence of brazed joints has exacerbated corrosion susceptibility since they have a tendency to emit electro galvanic currents with saliva and consequently release metal ions (Hwang et al. 2001). Berg et al. (1982) reported that austenitic stainless steel wires releases nickel and chromium in higher amounts than that of cobalt – chromium wires, resulting in discoloration, rust, or even breakages.

Clinical oral manifestations such as lesions produced from orthodontic retainers (Hawley appliance) with brazed joints have also been reported (Bishara, 1995). However, considering their short intra oral period it is assumed that this does not present any serious concerns.

Conversely to the assumed lack of concern, in general respectable leading orthodontic dental technicians from the local commercial industry (Claassen, 2002) have observed increased breakages in the brazed joints during short intra-oral periods. In their observations they have further noted the severity of the corrosion present on the brazed joints. This is an area of concern for dental technicians, since not withstanding the biological implications, there are several metallurgical implications, one of which that even though not assured, is nonetheless assumed that tensile strengths of the orthodontic SBSS will also be affected.

From a historical global perspective, increased susceptibility to corrosion with consequent release of metal ions may be instrumental in assessing the potential biological implications of the alloys (Eliades & Athanasiou, 2002). Therefore, by quantifying the effects of surface corrosion on the metal element (ions) content and tensile strength of orthodontic SBSS joints will help provide significant information to dental technicians and clinicians when planning patients' orthodontic treatment.

2.3 FACTORS INFLUENCING THE MICROSTRUCTURE OF SBSS JOINTS

2.3.1 INTRODUCTION

In order to fully understand the theory of corrosion susceptibility of orthodontic SBSS joints, it is imperative to understand the microstructural theoretical aspects as they impact on the corrosion behaviour of such alloys. McCabe (1990: 46) notes that metals in the molten state usually demonstrate mutual solubility in each other. According to McCabe (1990), the molten metal, when cooled to below its melting point, may result in the component metals:

- remaining soluble in each other (solid solutions)
- being completely insoluble in the solid state
- being partially soluble in the solid state
- forming intermetallic compounds with precise chemical formulation

This study employed alloys in which the metal components exhibited complete liquid solubility but limited solid solubility. Such alloys, termed “Eutectic”, are often used when lower fusion temperatures are desired as is in brazing (Anusavice, 1996: 336 and 337). The performance of silver solders is analogous to that of a eutectic alloy as they possess narrow melting ranges and melting points that are considerably lower than those of the parent metals. In considering these properties, silver solder may thereby be identified as a eutectic alloy.

The solidification process and grain structures of both the austenitic stainless steel wires and silver solder significantly influences the microstructure of orthodontic SBSS joints. The subsequent discussion therefore addresses these factors as they present potential problems in the Dental Technology industry.

2.3.2 AUSTENITIC STAINLESS STEEL WIRES AND SILVER SOLDERS: MICROSTRUCTURE AND METALLURGY

Several authors such as Eliades and Athanasiou (2002), Heidemann et al., (2002) and Bishara et al., (1993) have noted that the metallurgical knowledge of orthodontic alloys is fundamentally important for understanding the microstructural nature of orthodontic SBSS joints, as this instrumentally influences both its mechanical properties and its corrosion behaviour.

Austenitic 18-8 stainless steel wires (parent metal alloys) represent the alloys that are currently enjoying the most extensive and preferred use in orthodontic appliances because of their ability to withstand corrosion in the physiological milieu. The 18-8 stainless steel is so named because it contains approximately 18% chromium, 8% nickel and 0.2% carbon (van Noort, 2002: 282), thus forming a solid solution with the iron, which gives corrosion protection.

Chromium possesses the property of rendering the austenitic stainless steel to be passive by producing a tenacious layer of chromic oxide. This film formed on the surface of the alloy resists further attack from any aqueous media or when it is exposed to a mild oxidizing agent such as the oxygen in the air. Once this layer is formed no further oxidation will take place unless the layer is disturbed (McOrmand, 1996: 3-11). Nickel also contributes towards corrosion and helps strengthen the alloy (O’Brian, 1997: 67). For austenitic 18-8 stainless steel, the highest corrosion resistance is obtained at a passive film thickness of 3-5 nm, thereafter becoming amorphous in nature (Wranglen, 1985: 69).

A valuable feature for the use of austenitic stainless steel wires in orthodontics is that the wires braze easily (Williams, 1990: 372). Lower-melting point solders, such as silver solders (the filler metal), are preferable for brazing austenitic stainless steel wires as they improve the mechanical properties of orthodontic joints (Mc Ormond, 1996: 3-18 and confirmed by O’ Brien, 1997: 304). Silver solders are essentially alloys of silver, copper and zinc to which elements such as tin and indium may be added to lower fusion temperatures and improve solderability (Anusavice, 1996: 645)

Austenitic stainless steel softens at 1000°C, and between 400°C and 900°C there is a reduction in the resistance to corrosion of the parent metal. The reduction in resistance occurs because of recrystallization of the microstructure, changes in composition and the precipitation of chromium carbides at the grain boundaries that results in an intergranular corrosion or at least a partial disintegration of the metal grain boundary. This event often leads to a general weakening of the metal structure (Phillips, 1991: 540).

According to Sedricks (1996: 21) austenitic stainless steel wires containing in excess of 0.03% carbon will produce carbide precipitation on cooling at the austenite grain boundaries. This phenomenon is known as “sensitization”. This depletion in the chromium levels in austenitic steels is the result of non-equilibrium segregation during irradiation. In other words some constituents of the alloy migrate towards point “defect” sinks such as grain boundaries and dislocation lines, and other constituents migrate away. In dental technology, this is an area of concern as the brazing procedure employed could possibly augment orthodontic SBSS joint susceptibility to this phenomenon of “sensitization”. However in view of the above, austenitic stainless steel wires and silver solder remains the preferred choice**.**

2.3.3 THE SIGNIFICANCE OF THE FLUX EMPLOYED FOR ORTHODONTIC BRAZING

Fluxes are substances that are mixed with metal to aid in fusion. Globally, there are many types of fluxes available. Fluxes may be either borax or fluorides in nature. However, the flux used with stainless steel is a potassium fluoride flux. Orthodontic flux performs several important functions in the brazing process. According to McOrmond (1996: 3-19), fluxes serve to:

- protect the hot metal of the solder joint from oxidizing and removes oxides already on the metal.
- remove the passive layer on the surface of the metal so that the solder can bond.
- indicate the temperature to us informing us when the joint is hot enough to accept the solder.

Flux inclusions greatly influence microstructure of the brazed joints by producing porosities in the subsequent brazed seam. Therefore regardless of the brazing technique used, it is of primary importance to minimize the amount of flux used. Any excess flux remaining trapped within the filler metal will significantly alter the microstructure of the brazed surfaces and this contributes to the overall weakness of the brazed joints (Anusavice, 1996: 621).

2.3.4 TORCH FLAME SOLDERING AND ITS INFLUENCE ON THE MICROSTRUCTURE OF ORTHODONTIC SBSS JOINTS

Dental technicians involved in orthodontic work should be aware that the brazing temperatures for orthodontic silver solders are in the range of 620°C to 665°C (Anusavice 1996:645). This is crucial since the type of heat employed during brazing influences the microstructure of the austenitic stainless steel wires by the possible introduction of large gas pockets (Heidermann et al., 2002).

The theory of recrystallization of the grain structure due to overheating causes the chromium to react with the environment by forming carbides and consequently reducing the corrosion resistance, especially in aggressive environments. The silver solder, which in composition is a eutectic-type alloy, enhances this reduction and is thus a source of potential corrosion in orthodontic appliances with brazed joints (McCabe, 1990: 69). The brazing procedure employed with such solders may further contribute to a reduction in stainless qualities because of the electrogalvanic action between dissimilar metals.

There are several documented and recognised brazing techniques for orthodontic stainless steel wires, however the strongest brazed joints are produced by flame soldering techniques and the weakest brazed joints are produced by electric soldering methods (noted by Gardiner et al. as cited by Gawlik, 1996). This coupled with the stressful working conditions of the dental laboratory environment in terms of time and equipment costs, contributed in the torch flame soldering technique gaining popularity in industry. Much of the literature published on the strength of the SBSS joints, particularly by Combe (1992: 205), centres around the following practical points:

- It is essential that the metallic parts to be joined are thoroughly clean.
- A solder of the correct fusion temperature should be selected.
- The reducing zone of the flame is used.
- The flame should be removed from the solder as soon as it flows.
- Immediately after soldering the work is quenched in water.

Heidermann et al. (2002) also reported that the flame soldering technique may yield the best results in terms of outward appearance, mechanical stability and corrosion properties if temperature and soldering time in particular are kept within close tolerances. Dental technicians are to heed this advice if quality orthodontic SBSS joints with minimised microstructural changes are to be produced.

2.3.5 MICROSTRUCTURAL CHANGES RESULTING FROM QUENCHING

Solidified SBSS joints consisting of a mixture of insoluble metals (polycrystalline) often possess the potential for the establishment of electrolytic cells on their surfaces thereby reducing the resistance to corrosion (McCabe, 1990: 59). This reduction can be avoided or minimised by rapidly cooling from a high temperature (quenching).

After quenching, the solidification process that follows is one of crystallization and is initiated at specific sites called nuclei. Nuclei are generally formed from impurities within the molten mass (McCabe 1990: 43). Confirmed by Jochen et al., (1988), quenching as opposed to bench cooling usually results in a finer grain structure by producing more nuclei of crystallization and more grains in a given volume of material. This contributes to increase strength and hardness (Combe, 1992: 38).

Rapid cooling to room temperature allows for certain degree of carbon to be precipitated. However, room temperature austenite continues to be largely saturated with carbon, resulting in the formation of envelopes of chromium-depleted austenite around these carbides. Cooling rates therefore primarily influence the microstructural size of the developed phases in orthodontic SBSS joints (Zinelis, 2004) and this in turn influences corrosion behaviour.

2.4 CORROSION OF ORTHODONTIC SBSS JOINTS

Corrosion occurs because of the inherent tendency for most metals to return to their natural state. According to Kusy (2000), passivated materials such as stainless steel will corrode like other metallic alloys if their protective oxide layers are stripped away and prevented from reforming. The corrosion potential of the material is further increased and compounded when placed in aggressive environments. This results in weakening and eventual fracture of the material. The corrosive products produced may also react adversely. This latter factor is of major concern. The knowledge gained from the preceding discussions on microstructure will thus help in facilitating an understanding on the corrosion behaviour of orthodontic SBSS joints.

2.4.1 GALVANIC CORROSION OF ORTHODONTIC SBSS JOINTS

Corrosion is described as an electrochemical process that results in the loss of the essential metallic properties of the metal. When two metals are connected together in a conducting solution or electrolyte, the more electronegative or base metal of the bimetallic couple will be the anode and corrode. The more electropositive or noble metal will function as the cathode (von Fraunhofer, 1997).

According to Aromaa and Klarin (1999: 128 and 129) the electron flow in the galvanic couple causes the more active and nobler members to polarize and their potentials to approach each other. Passive 18-8 austenitic stainless steel encourages polarization in the passive state to easily occur. If the potential of the more noble material changes easily, the shift of the more active material is small and galvanic corrosion is not as great. If the potential of the noble material does not change easily, the potential of the more active material changes significantly and galvanic corrosion becomes appreciable. The extent of galvanic corrosion therefore depends on the corrosion potentials and uniform corrosion rates of the metals, relative surface areas of active and passive metals, and the conductivity of the electrolyte.

As noted earlier, an electric couple may exist between the dissimilar metals in the mouth, if significant differences exist in the potential between the silver solder and the stainless steel materials. Saliva contains salts that serve to form a weak electrolytic couple (Anusavice, 1996: 352). The brazing of stainless steel wires with silver solder could therefore reduce the stainless steel passivity, because of the electrogalvanic action between the two dissimilar metals (Craig, 1997: 422). The silver being the more anodic material usually corrodes and this is called *bimetallic* or *galvanic* corrosion. Such corrosion is of concern to dental technicians as it is generally associated with the observed deterioration of orthodontic SBSS joints in the oral cavity.

2.4.2 THE IMPORTANCE OF THE GALVANIC SERIES IN GALVANIC CORROSION AND HOW IT DIFFERS FROM THE EMF SERIES

At least a decade ago, a convenient galvanic chart was devised that ranked materials according to their noble metal or base metal characteristics (Kusy, 2000). As a recognized reference, the galvanic series (Fontana, 1987: 42 - Appendix A), yields a much more accurate prediction than the EMF series since it reflects an order of corrosion tendencies.

The recognized galvanic series was augmented by experience and it is believed that the knowledge gained will help provide general information to dental health professionals on the behaviour of dissimilar metal combinations (austenitic stainless steel wires and silver solder).

However, unlike the galvanic series, the EMF (electromotive force) classification is an arrangement of the elements in the order of their dissolution tendencies in water (Anusavice, 1996: 351). Here the potential between metals exposed to solutions containing approximately one gram atomic weight of their respective ion (unit activity) are precisely measured at a constant temperature and hence classified as the EMF series (Fontana, 1987: 42 - Appendix A).

According to Anusavice (1996: 351) the standard potential may be considered as the voltage of electrochemical cells in which potentials are referenced against the hydrogen electrode, designated arbitrarily as zero. Potentials between metals are determined by taking the absolute differences between their standard EMF potentials. Metals with a more positive potential have a lower tendency to dissolve in aqueous environments and those with the lowest electrode potential goes into solution. The strength and direction of the current thus depend primarily on the electrode potential of the individual metals.

The relative position of any of the elements in the electromotive series is dependent not only on the inherent solution tendencies but also on the effective concentration of ion of that element that are present in the environment. The EMF series provides information only about whether a given corrosion reaction can occur and does not predict neither the occurrence nor the rate of corrosion (Anusavice, 1996: 352). Therefore, the galvanic series is received much more favourably.

Tretheway and Chamberlain (1995: 136) reported that the galvanic series:

- is a relative qualitative series listing an experimental order of nobility (or activity) of metals.
- contains both pure metals and alloys and this serves as a considerable practical advantage.

- is measured under arbitrary (through specified) conditions of temperature, pressure and electrolyte.

The farther apart the metals in the galvanic series (Appendix A) are the greater will be the galvanic rate. Metals or alloys at the upper end are *noble* while those at the lower end are *active* (Corrosion Control and Treatment Manual Online, 2000-10-27). It should be noted that although the galvanic series does not provide information on the initial polarization behaviour or long-term behaviour in contact between dissimilar galvanic couples, it does however, afford any dental technician to gain a better perspective on the galvanic corrosion tendencies of orthodontic SBSS joints.

2.4.3 THE RELEVANCE OF ACTIVE – PASSIVE CELLS TO GALVANIC CORROSION

Inhomogeneities such as secondary phases present in the composition of the brazed joint produce defects that will disturb the passive layer of the joint, (Wranglen 1985: 94). Austenitic stainless steel depends on this tightly adhering passive film (usually an oxide) for corrosion protection. The corrosion action usually starts as an oxygen concentration cell; e.g. salt deposits on the metal surface in the presence of water containing oxygen can create the oxygen cell.

If the passive film is broken beneath the salt deposit, the active metal beneath the film will be exposed to corrosive attack. An electrical potential will develop between the large area of the cathode (passive film) and the small area of the anode (active metal) resulting in rapid pitting of the active metal, (Corrosion Control and Treatment Manual Online, 2000-10-27).

According to Eliades (2002) austenitic stainless steel wires are characterized by passive–active behaviour depending on the environmental conditions in which the protective chromium oxide layer may be eliminated (active form) or regenerated (passive form). Thus, galvanic corrosion may take place depending on the stainless steel wire and solder combination arising from brazing.

2.4.4 PITTING CORROSION

A negative consequence to the brazing procedure employed by dental technicians is the potential for pitting corrosion to transpire. When the breakdown potential of an alloy is reached, the oxide layer dissolves and the onset of surface corrosion and pitting begins (Kim et al., 1999). Pitting corrosion appropriately described by Frankel (Pitting Corrosion of Metals Online, 2004-07-30), is a localized accelerated dissolution of metal that occurs as a result of a breakdown of the otherwise protective passive film on the metal surface. If the attack initiates on an open surface, it is called pitting corrosion as opposed to crevice corrosion that occurs at an occluded site (Pitting Corrosion of Metals Online, 2004-07-30).

Pitting corrosion is almost always initiated by:

- some chemical or physical heterogeneity at the surfaces such as an inclusion, second phase, solute-segregated grain boundaries, flaws, mechanical damage, or dislocations (Pitting Corrosion of Metals Online, 2004-07-30).

- low dissolved oxygen concentrations (which tend to render a protective oxide film less stable) and high concentrations of chlorides (Corrosion-doctors Online, 2004-07-30).

In a preliminary study (part one, 2001, unpublished – Appendix C), the combined effects of dissimilar metals and the high chloride ion content of the electrolyte produced extensive corroded orthodontic SBSS joints. An electrical potential developed between the large areas of the cathode (passive films) and the small areas of the anode (active silver solder). The presence of the chloride ions combined with oxygen or oxidizing salts resulted in the passive film breaking beneath the salt deposit and thus exposing the active silver solder to severe corrosive attack. Consequently, rapid pitting corrosion of the active silver solder, a common mode of galvanic corrosion, resulted.

Microscopical examination further confirmed that failure of the orthodontic SBSS joints increased with the presence of large visible corrosion pits. Lakatos-Varsanyi et al., (1997) suggested that if chloride ions are present in the passive layer, this weakens the film and thereby initiate pitting corrosion. Ryan et al., (2002) reported that the random and sporadic pitting process causes localized dissolution of an oxide-covered metal in specific aggressive environments.

According to Sedricks (1996: 134) the pitting potential of certain weld (brazing) metals are significantly more active and are prone to preferential attack as opposed to the parent metal. Taking this point into consideration together with the fact that pitting corrosion is mostly associated with a high prevalence of chloride ions, it is suggested that pitting corrosion of orthodontic SBSS joints possibly results from the combined effects of:

- Improper heating during fusion of the solder or from improper fluxing during heating of the solder (Craig, 1997: 400),
- The presence of electrogalvanic currents and
- The chloride-containing solution that encourages the susceptibility to pitting corrosion (Johnson, 1995: 484).

2.4.5 THEORY OF CORROSION PIT SHAPE AND GROWTH: IN BRIEF

An understanding on pit shape and growth is crucial as it lends itself when discussing the phenomenon of pitting corrosion and when interpreting scanned images of pits. Frankel (Pitting Corrosion of Metals Online, 2004-07-30) reaffirms the theories of past authors who have noted that the aggressive anionic chloride ions are relatively small with a high diffusivity thereby interfering with the passivation and is thus ubiquitous as a contaminant. The autocatalytic and insidious nature of pits is such, that once they are initiated they provide conditions for promoting further pit growth.

An illusion of a porous cover is often created when attempting to examine corrosion pit growth. In orthodontic SBSS joints this porous cover could possibly be a precipitated product layer that makes visual detection extremely difficult and almost impossible as they remain reflective. As a result the awareness on the severity of the attack is often overlooked and this enhances failure (Pitting Corrosion of Metals Online, 2004-07-30).

Corrosion pits can be either hemispherical or cup shaped and they usually grow in the direction of gravity. For ease of reference, Figure 2.1 shows the two types of pit groups namely "*trough"* and "*sideway"* pits and their common pit profiles (Corrosion-doctors Online, 2004-07-30 and Aromaa & Klarin, 1999: 144).

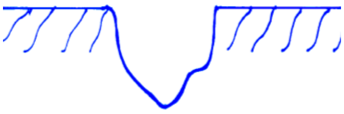
The contentious issue surrounding pit growth and development has been an on-going discussion since, as noted previously, the detection of pitting corrosion represents a major challenge to the extent of which several speculative models in terms of detecting and monitoring of pitting corrosion have been proposed. In order to remain within the focus of this research, very briefly, corrosion pits that tend to grow so as to perforate the metal are developed only during the chloride corrosion pitting. This occurs at potentials where the passive film is otherwise stable (Hisamatsu et al., 1994).

TROUGH PITS:

Narrow, deep

Shallow, wide

Elliptical



Vertical Microstructural Orientation

SIDEWAY PITS:

Subsurface

Undercutting

Horizontal Microstructural Orientation

FIGURE 2.1: Two Groups of Corrosion Pits and their common shapes

However, if and when the breakdown of the passive film does occur it generally involves the transport of the aggressive anions through the passive film to the metal/oxide interface where aggressive dissolution is promoted. The rapid dissolution of metal within the pit tends to produce an excess of positive charge in this area, resulting in the migration of chloride ions to maintain electroneutrality and this entire process accelerates with time (Fontana, 1987: 68). This is consistent with the large body of corrosion theories documented in the literature particularly by Ryan et al., (2002).

2.4.6 INFLUENCE OF CORROSION ON THE STRENGTH OF ORTHODONTIC SBSS JOINTS

The preceding discussions have noted the susceptibility of orthodontic SBSS joints to corrosion because of a galvanic couple being created. Studies in the past two decades (Angelini et al., 1991; Gjerdet & Hero, 1987, Berge et al., 1982) have concentrated on the amount of corrosion found on various combinations of stainless steels and brazing techniques. However, little has been reported on the effect of corrosion on the strength of the brazed joints.

The strength of orthodontic stainless steel wires, and their silver brazed joints, is crucial to the success of an active orthodontic appliance. As no union takes place between solder and the stainless steel wire, the result may be the premature fracture of the SBSS joint, especially under the conditions of stress, strain and action of the oral environment (Adams, 1984: 189).

As previously emphasized, austenitic 18-8 stainless steel wires depends on the passive film produced by the chromium in order to gain the corrosion resistance property. The rate at which corrosion of SBSS joints occurs is influenced by the composition of the materials used, the chemical and thermal environment of the material, the surface area and the degree of surface smoothness (Bishara et al., 1993).

A rough surface accumulates plaque and causes further corrosion by the formation of a concentration cell in the mouth (Shigeto et al., 1991). This was later confirmed by a clinical examination by Bishara, (1995).

Bourauel et al., (1998) recommends that manufacturers of orthodontic wires should make concerted efforts to help improve the surface quality of their products as this ultimately affects the corrosion behaviour the joints. It is therefore widely advocated that in order to reduce the susceptibility to corrosion, the surface of the SBSS joints be polished, since pores, inhomogeneities and poorly trimmed surfaces encourage corrosion in any aqueous electrolyte systems such as the oral environment (Heidemann et al., 2002).

2.5 AN OVERVIEW OF AQUEOUS ELECTROLYTE SYSTEMS

The foregoing literature has necessitated that knowledge on aqueous electrolyte systems simulating mouth conditions is required, in order to fully understand the study at hand. Aqueous electrolyte systems used for in vitro studies should meet the basic principal requirements and ideally simulate in a manner similar to that of natural saliva. Leung & Darvell (1997) documented that due to the inconsistent and unstable nature of natural saliva it is impossible to duplicate the exact properties of human saliva.

The electrochemical properties of saliva depend on its composition, namely the surface tension and buffering capacity; all of which influence the magnitude of the corrosion process. The bicarbonate ion, which is a by-product of cell metabolism, acts mainly to buffer and influence the pH of saliva. It is during eating, that saliva flow is raised, and the increased secretion ensures that there are enough bicarbonate ions to buffer the acid produced by plaque bacteria (Oral Environment Online, 2000-10-27).

A significant point is that the electrolyte composition affects the distribution of galvanic corrosion on the anodic metals. High electrolyte conductivity produces uniform distribution of the less noble metal with the total weight loss being high. Low electrolyte conductivity, galvanic corrosion of the less noble metal become concentrated primarily around the bimetallic junction and the total weight loss of the anode decreases (Pryor & Astley, 1994: v1: 229)

Practically and economically it is impossible to collect a pool of whole saliva from a large number of individuals without further complications. The proceeding discussion therefore demonstrates the deciding factors influencing the aqueous electrolyte system selected for use in this study.

2.5.1 SELECTION OF THE AQUEOUS ELECTROLYTE SYSTEM FOR THIS IN VITRO STUDY

Without divulging too much information on the preliminary studies performed by the researcher (2001 and 2002, unpublished) as the consecutive chapters do address this further, a very brief reference to the preliminary studies is nonetheless made in order to help provide the sequence of events that resulted in the decision of the selected electrolyte for this study. Orthodontic SBSS joints were initially immersed in Ringer’s solution. However, premature failure and increased corrosion activity resulted due to the combined effects of dissimilar metals and the high salt content (chloride ions) of the Ringer’s solution.

For the preliminary study- part two, references to previous studies were made and the comportion of artificial saliva and Ringer’s solution were documented as follows:

PREVIOUS STUDIES (YEAR)	SOLUTION
Laurent et al., **(2001)**	Fusayama's artificial saliva
Meiana and Takahashi, **(1998)**	artificial saliva
Lakatos-Varsanyi et al., **(1997)**	artificial saliva
Downing et al., **(1995)**	artificial saliva
van der Bijl & de Waal, **(1994)**	artificial saliva
Angelini et al., **(1991)**	artificial saliva and Ringer's solution
Brockhurst and Pham, **(1989)**	0.9% NaCl in water
Engelbrecht, **(1984)**	Fusayama's artificial saliva
Berge et al., **(1982)**	0.9% NaCl and Ringer's solution
Mueller, **(1981)**	% 1 Hydrogen peroxide and artificial saliva

In view of the above, the preliminary investigation – part two performed by the researcher (2002, unpublished – Appendix C), Fusayama's artificial saliva (Fusayama et al., 1963) was the electrolyte used. Minimisation of orthodontic SBSS joint failures was demonstrated and therefore, Fusayama's artificial saliva was selected as the electrolyte for the final study.

2.5.2 FUSAYAMA'S ARTIFICIAL SALIVA

Fusayama's artificial saliva is an aqueous solution of the chlorides of sodium, potassium and calcium. Mucin based Fusayama's artificial saliva produces results that most closely approximate those in natural saliva (noted by Meyer and Nally and as cited by Leung and Darwell, 1997).

In natural saliva, the antibacterial function performed by the secreted sulphated glycoproteins, the mucins, serve as a trap to aggregate bacteria, which are eventually swallowed. The same mucins provide a thin lubricating film over the mucous membrane and teeth to serve as lubricants (Harris and Christen, 1982: 249). This was later confirmed by Ganong (2001: 473).

Mucins are also the principal organic constituents of mucus, the slimy visco-elastic material that coats all mucosal surfaces. Specific protective functions include:

- protection against desiccation and environmental damage,
- lubrication,
- antimicrobial effects against potential pathogens and
- buffering effects as they contain moderate quantities of bicarbonate ions, which specifically neutralize the acids (Tabak et al., 1982 and Guyton, 1991: 711).

Recent clinical studies on patients with deficient salivation (xerostomia) have further confirmed that mucin-based artificial saliva had the best wetting properties than carboxymethylcellulose (CMC)-based artificial saliva. CMC is often used as replacements for the gylcoproteins occurring in human saliva (van der Bijl & de Waal, 1994) and is a common ingredient used to impart lubrication and viscosity (Aydin et al., 1997).

However, unlike CMC-based artificial saliva that is completely different, the rheological properties of mucin-based artificial saliva compare favourably with those of human saliva. Vissink et al., (as cited in Downing, 1995) studied the rheological properties of saliva substitutes containing mucin and carboxymethylcellulose. They concluded that artificial saliva containing mucin (bovine submandibular or pig gastric mucin) qualitatively approached the visco-elastic properties of human saliva, and therefore the best substitute for human saliva. Mucin-based artificial saliva may also improve the quality of life for xerostomia patients (Aydin et al., 1997). More importantly, in vivo studies have shown that there are no significant effects on corrosion behaviour arising from mucin present in the proteins found in the mouth (von Fraunhofer 1994: v2: 159)

The foregoing literature review has identified microstructural changes associated with orthodontic SBSS joints, which encourage their susceptibility to corrosion. Such corrosion characteristics of dental metals are a concern because in the mouth the presence of such corrosion tendencies may cause health hazards, weakening and deteriorating the longevity of the SBSS joints (Bishara, 1995). In addition, the microbiological characteristics of the oral cavity are also known to provide a suitable environment that promotes the corrosion of metals (Eliades et al., 2002).

At present removable orthodontic retainers such as the Hawley appliance (Plate 2.1) are used for three months after the active phase of orthodontic treatment to stabilise the already mobile teeth. By investigating the timeframe over which orthodontic SBSS joints are physically compromised, in terms of their microstructure and strength, may provide valuable information to dental manufacturers of silver solders, and thereby positively influence its use by other dental health professionals.

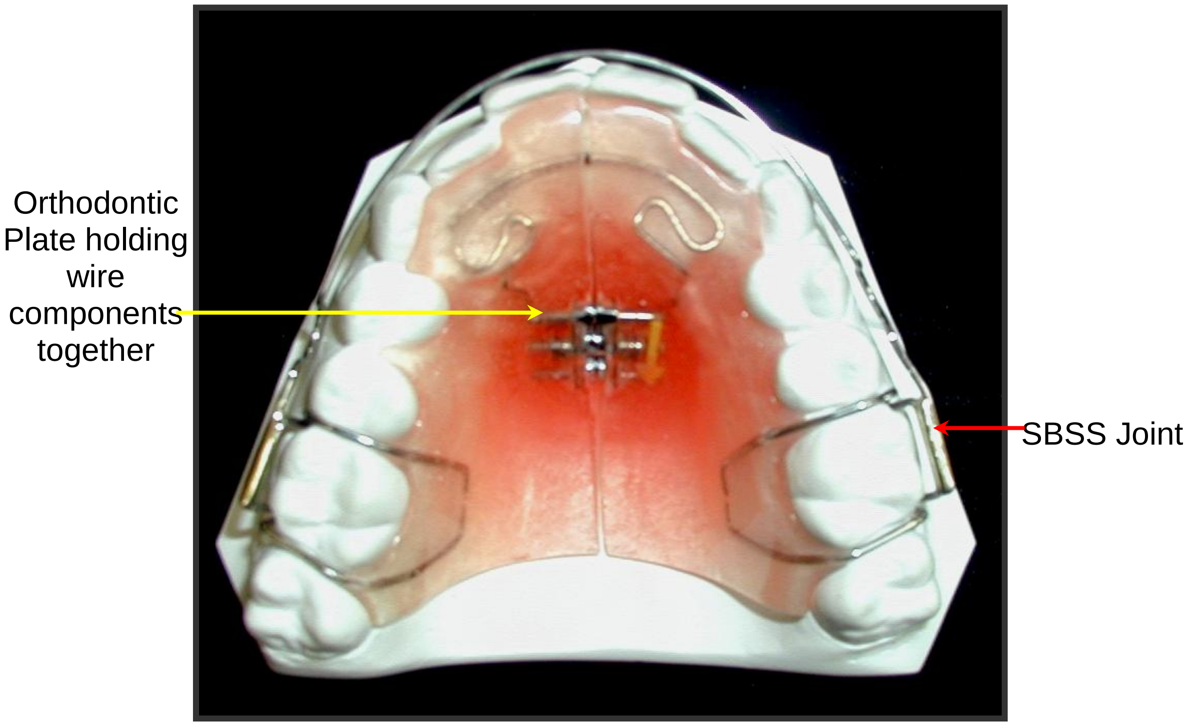


Plate 2.1: Orthodontic Hawley Appliance

CHAPTER THREE

If we knew what we were doing, it wouldn't be called research, would it?

Albert Einstein (1879 – 1955)

METHODOLOGY

3.1 THE DATA

3.1.1 PRIMARY DATA

The following primary data were obtained in order to determine:

1. Tensile strength of orthodontic SBSS joints using a tensile testing machine.
2. Extent of the surface corrosion and the metal element (ions) content of the fracture using scanning electron microscopy and energy dispersive spectroscopy.
3. The association between the exposure periods and microstructure of orthodontic SBSS joints.

The following detailed analysis regarding the orthodontic SBSS joints were conducted:

- The mean tensile strength values of all four sprayed sample groups.
- The mean tensile strength values of the control sample group.
- The association between microstructure, tensile strengths and exposure periods.
- The difference in colour and the rate of corrosion products produced of all sample groups, determined by visual interpretation.
- The difference in microstructure of all five sample groups as determined microscopically.

Data were analysed using the one-way ANOVA statistical method and the Multiple Linear Regression analysis.

3.1.2 SECONDARY DATA

- In order to ensure the in vitro machine simulated oral conditions as in the mouth, the American Standard of Materials (ASTM) B117 (1995) was used.
- As a guide in determining the suitable cross head speed for tensile testing, the ISO 9333 (1990: 3) (Tensile strength) was consulted.

3.1.3 THE CRITERIA GOVERNING THE ADMISSIBILITY OF THE DATA

(i) Only orthodontic SBSS joints made by the researcher in the dental laboratory at the Dental Services Department, Steve Biko Campus (Durban Institute of Technology, Durban, South Africa), were used.

(ii) Only data produced by the Tensile Testing machine (LLOYD LR 30K), Mechanical Engineering Department, Steve Biko Campus (Durban Institute of Technology, Durban, South Africa), were used.

(iii) Only analytical data produced and recorded on the

- scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) system (SEM Hitachi S520 Scanning Electron Microscope and LEO 1450), SEM Unit, Howard College (University of KwaZulu-Natal, Durban, South Africa),

- scanning electron microscope and energy dispersive spectroscopy system (Phillips XL30 Scanning Electron Microscope), Centre for Electron Microscope, Pietermartizburg Campus (University of KwaZulu-Natal, Pietermaritzburg, South Africa),

- stereo light microscopes (LEICA MZ 8), Centre For Materials Engineering, Mechanical Engineering Department (University of Cape Town, Cape Town, South Africa),

- research light microscopes (REICHERT MeF3A), Centre For Materials Engineering, Mechanical Engineering Department (University of Cape Town, Cape Town, South Africa),

- scanning electron microscope and energy dispersive spectroscopy system (LEO S440 Scanning Electron Microscope), SEM Unit, (University of Cape Town, Cape Town, South Africa), were used.

Prior to reading the following section, cognizance of preliminary study - part one and preliminary study - part two (Appendix C) should be taken into account, as these studies significant influenced the following methodology.

3.2 METHODOLOGY

This study used the pre-test and post-test experimental methods. Initially, the in vitro machine and electrolyte used validated the complete immersion of the orthodontic SBSS joints (Preliminary Study: Part One, Appendix C). However, preliminary study: part one produced no measurable data. The pioneering of the in vitro machine thus necessitated a preliminary study: part two (Appendix C) to re-address the methodology and to re-modify the in vitro machine. In the preliminary study: part two, data was produced thereby showing that the procedures employed were sound. In the final experiment, the modified in vitro machine help established the levels of predictability and strength, and parameters were established such that comparisons could be made.

3.3 SAMPLE SIZE

The central limit theorem states that for sample sizes greater than 30 the sampling distribution of the mean has a normal distribution and therefore a sample that is equal to or greater than 30 is recommended for the purpose of valid statistical analysis.

Having completed two preliminary investigations and with the increasing constraints in time and budget, it was therefore decided that the maximum affordable sample size of 20 be used for each experimental group that had removal periods at 7, 14, 21 and 28 days simultaneously.

The ensuing section provides a detailed description of the materials and methods employed taking into account the outcomes observed in the two preliminary investigations, in order to conduct this study.

3.4 SELECTION OF ORTHODONTIC MATERIALS

The selection of orthodontic materials used in this study was based primarily on their popularity in Durban particularly at the time of the telephonic survey (2000), availability and ease of production (not technique sensitive). The telephonic survey (Table 3.1) identified the orthodontic brand materials commonly used by dental technicians when fabricating removable orthodontic appliances. Cost was also considered and this significantly influenced the marketing and consequent acceptance of the elected Remanium® (Dentaurum, Pforzheim, Germany) materials into the Dental Technology field.

Remanium® 0.7mm gauge orthodontic stainless steel wire (Dentaurum, Pforzheim, Germany), corresponding silver solder material by Dentaurum (Pforzheim, Germany) and Dentaflux universal soldering flux (Dentaurum, Pforzheim, Germany, Plate. 3.1) were the selected materials used to produce the specimens.

Plate 3.1: Orthodontic Armamentarium:
(a) Soldering Flux, (b) Remanium 0.7mm wire, (c) Silver Solder

Table 3.1: Telephonic Survey on the popular orthodontic brand materials used by dental laboratories and teaching institution when fabricating removable orthodontic appliance

BRAND NAME OF WIRE	RECOMMENDED SOLDER (BRAND NAME)	RECOMMENDED FLUX	AVAILABLE	COST	REASONS FOR USE
REMANIUM	Silver Solder (Dentaurum)	Dentaflux Dentaurum	✓	*☺	Very popular due to availability, low cost and ease of brazing.
KC SMITH	Gold Solder or Silver Solder (KC Smith)	KC Smith flux	✓	**😐	Popular, similar characteristics to Remanium. However slightly more expensive and if gold solder used, cost accelerates.
SCHEU	PD Solder with inert flux	Flux not required	✓	**☹	Very expensive hence not popular
LEWA			✗	👎	Failed selection as wire is not supplied in 0.7mm

KEY

* - Cheapest ☺

** - Slightly more expensive and cost accelerates with use of gold solder 😐

*** - Most expensive ☹

Table 3.2 shows the chemical composition of metal elements in weight %, as provided by the dental manufacturer, present in the orthodontic stainless steel wires, silver solder and the liquid flux (Dentaurum, Pforzheim, Germany).

Table 3.2: Metal Element Content of Orthodontic Materials (Dentaurum, Pforzheim, Germany)

CHEMICAL		**Wire %**	**Solder %**	**Flux %**
Carbon	**C**	0.05-0.15		
Silicon	**Si**	≤2.0		
Chromium	**Cr**	16.0–19.0		
Manganese	**Mn**	≤2.0		
Molybdenum	**Mo**	≤0.8		
Phosphorus	**P**	≤0.045		
Nickel	**Ni**	6.0-9.5		
Nitrogen	**N**	≤0.11		
Iron	**Fe**	remainder		
Copper	**Cu**		22	
Zinc	**Zn**		17	
Silver	**Ag**		56	
Tin	**Sn**		5	
Potassium hydroxofluoroborate				60-80
Boron	**B**			1-5

3.5 PREPARATION OF SAMPLES

Remanium® 0.7mm gauge orthodontic stainless steel wires (Dentaurum, Pforzheim, Germany) are supplied in the form of wire rolls (Plate 3.1). With a pair of cutting pliers the stainless steel roll was therefore cut into lengths of 40cm pieces. A length of 40cm sufficiently allowed for the wires to:

- conform to the shape of the clamping jigs (Plate 3.2),
- maintain distance between the clamping jigs during separation on the tensile testing machine, and
- minimise other stresses such as fatigue stresses from being exerted on the wire during tensile testing.

With the use of the bending jig the stainless steel wires were bent to ensure accurate dimensions (Plate. 3.2)

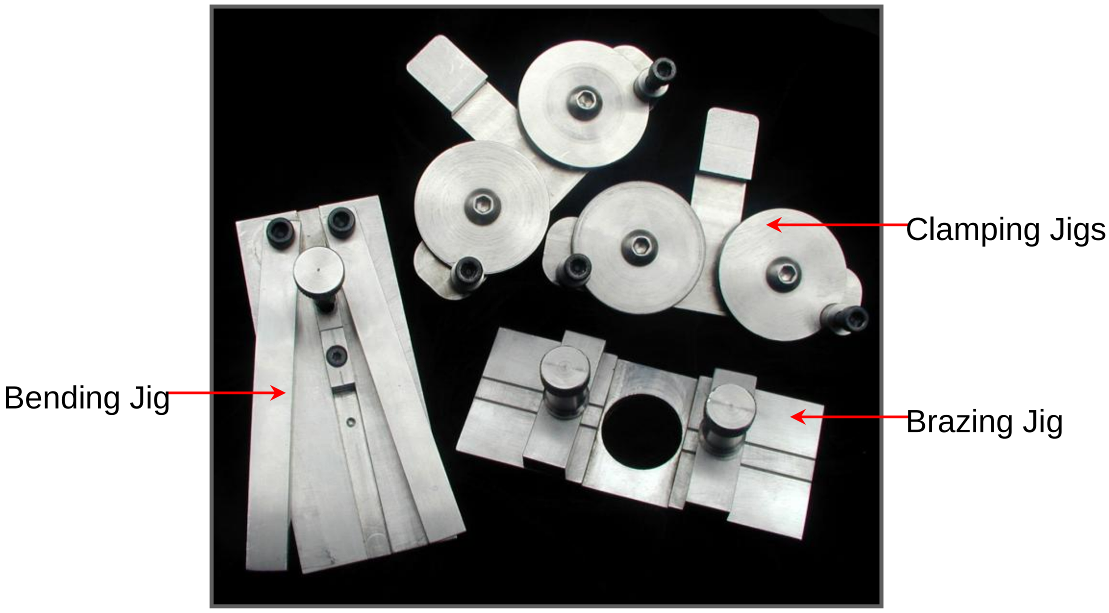


Plate 3.2: Orthodontic Jigs

3.6 BRAZING OF ORTHODONTIC SBSS JOINTS

In order to establish the tensile strengths of the orthodontic SBSS joints, 20 specimens for each sample group for each time period at 7, 14, 21 and 28 days, and 20 for the control group were fabricated (20 x 4 sample groups + 20 control group where n=100 specimens).

Studies undertaken by O'Toole et al., (1985) and Gawlik et al., (1996) reported that the reducing flame from a hand held butane torch produces joints with significantly higher tensile strengths. This technique was used for the brazing process in this experiment.

To ensure uniform and precision brazing, the wires were held in a more accurate registration and were then brazed on the brazing jig (Plate 3.2) using silver solder and liquid flux (Dentaurum, Pforzheim, Germany) as the brazing media. This further minimised any surface flaws at the junction of the solder and wire interface, as this ultimately affects the strength of the orthodontic SBSS joints.

It must be noted that prior to application of the brazing media, the stainless steel wire surfaces were wiped cleaned to remove any dirt and impurities that may have been present. According to Cary (1986: 4490) the property of flux is that of protection and not cleaning, therefore proper cleaning of the parent metals prior to flux application must be done.

The brazing jig supporting the two stainless steel wire pieces with the painted flux and silver solder between them were heated with the gas-air butane torch until the silver solder flowed and an effective sandwich union was achieved. To prevent overheating of the stainless steel wires followed by carbide precipitation and softening of the wires (O'Brien, 1997: 305), the flame was removed as soon as the solder flowed along the wires.

After brazing, a plastic dropper containing water at room temperature was used to quench the samples. Quenching prevents the embrittlement of the solder by age hardening (O'Brien, 1997: 305). The orthodontic SBSS joints were then lightly rubber wheeled to remove any excess solder thereby producing smooth and highly polished surfaces.

3.7 INCLUSION CRITERIA OF ORTHODONTIC SBSS JOINTS

The following criteria assisted the researcher in ensuring all specimens produced were the same thereby improving the reliability of this study:

- The orthodontic stainless steel wires (in the area of the joint) were completely covered by the silver solder after the brazing process.
- Only those specimens conforming to the correct dimensions, and allowed for the desired orthodontic silver brazed stainless steel "bridge" joint length of an Adams clasp® of 8 mm (Plate 3.3), was accepted in the study.
- All specimens had smooth, clean and highly polished joint surfaces.

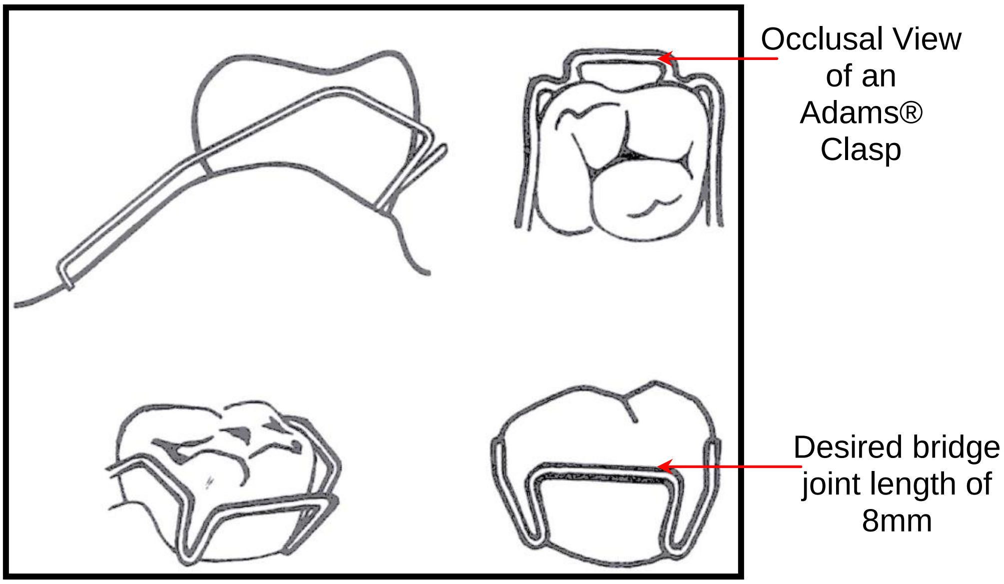


Plate 3.3: Adams® Clasp

(As sited in Dickson and Wheatley, 1978: 25)

3.8 ARRANGEMENT OF ORTHODONTIC SBSS JOINT SPECIMENS IN THE IN VITRO MACHINE

The orthodontic SBSS joint specimens meeting with the requirements of the inclusion criteria were then assembled in perspex stands (Plate 3.4). Each stand, numbered 1 – 4, received 20 SBSS joint specimens. Any contact between the specimens was avoided (ASTM Standard, 1995: B117, Appendix B). This minimised the potential of the galvanic cell evidently present as a result of the dissimilar metals of the brazed specimens.

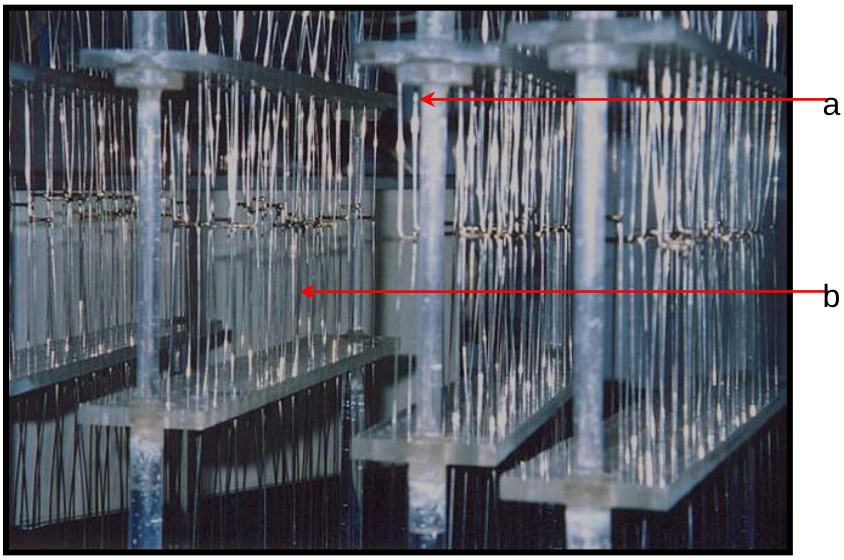


Plate 3.4: Orthodontic SBSS specimens in perspex stands:
(a) Perspex stand, **(b)** Assembled Orthodontic SBSS specimen

Once assembled, the Perspex stands were readily placed into the in vitro machine. Perspex stand 1 was positioned in the in vitro machine to the side closest in relation to the green gas cylinder (Plate 3.5/a). The subsequent placement of the stands 2, 3 and 4 followed. Perspex stand 4 was therefore closest to the ultraviolet light (Plate 3.5/c). Numbering the perspex stands guided the removal from and insertion into the machine when procedures simulating mouth conditions were followed.

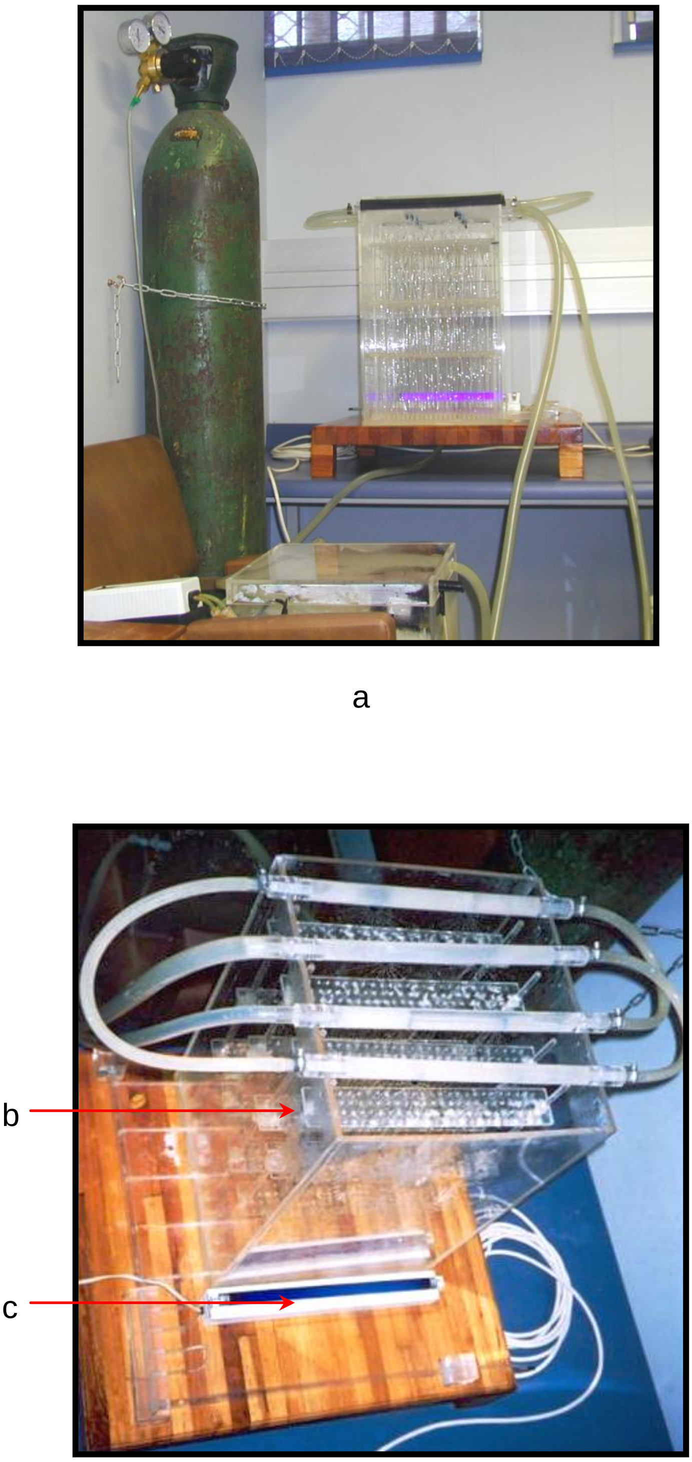


Plate 3.5: **Arrangement of perspex stands in the exposure chamber of the in vitro machine:**

- **(a)** Full view of the in vitro machine,
- **(b)** Exposure chamber,
- **(c)** Ultraviolet light

Furthermore each perspex stand, containing the assembled SBSS specimens, was designated a rod spraying artificial saliva via. nozzles (Plates 3.6) such that direct impingement of the spray on the SBSS specimens was avoided, (ASTM Standard, 1995: B117, Appendix B).

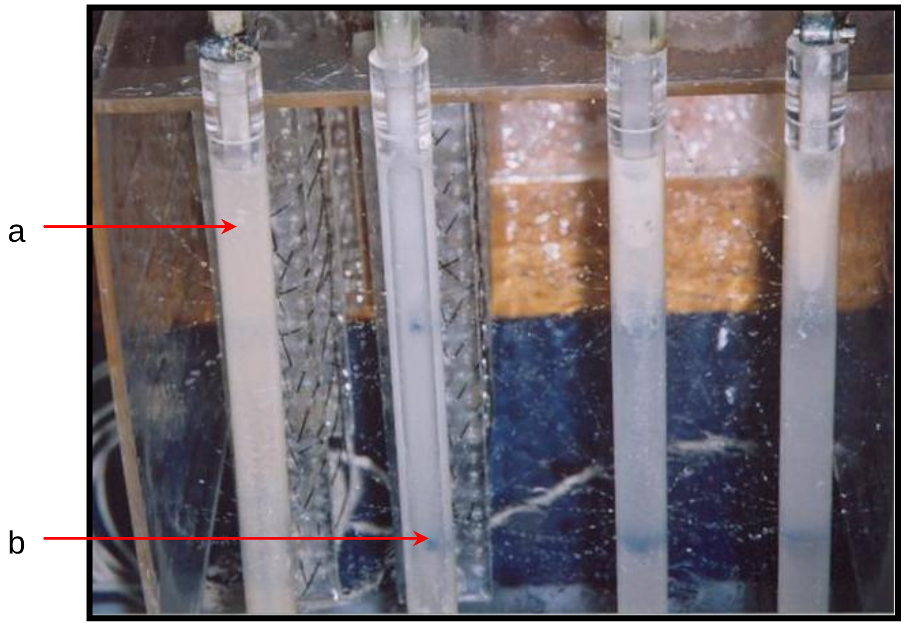


Plate 3.6: **Designated Rods with nozzles spraying artificial saliva on orthodontic SBSS specimens:**

(a) Rods containing artificial saliva,

(b) Blue nozzle spraying artificial saliva

3.9 THE IN VITRO MACHINE

The in vitro machine consisted of two chambers. The larger chamber known as the exposure chamber, contained all 80 specimens and accommodated a sprinkler system that sprayed Fusayama's artificial saliva on the orthodontics SBSS specimens. The placement site of the 80 specimens in the exposure chamber as previously stated was noted by numbering the Perspex stands housing the SBSS joints. Ultraviolet light was placed near the exposure chamber as a precautionary measure against bacterial contamination.

The smaller reservoir contained the artificial saliva, which was cyclically re-pumped to the exposure chamber (Plate 3.7). Fusayama's artificial saliva in the reservoir was heated by means of an immersion heater, and the temperature set at 37°C. A regulated flow of carboxygen (95% oxygen and 5% carbon dioxide) was also bubbled into the saliva. The saliva entering the atomisers (nozzles) was filtered to remove all impurities, (ASTM Standard, 1995: B117). The saliva was changed weekly to overcome any loss of liquid due to evaporation and aeration of the sprayers as experienced in the preliminary investigation – part two.

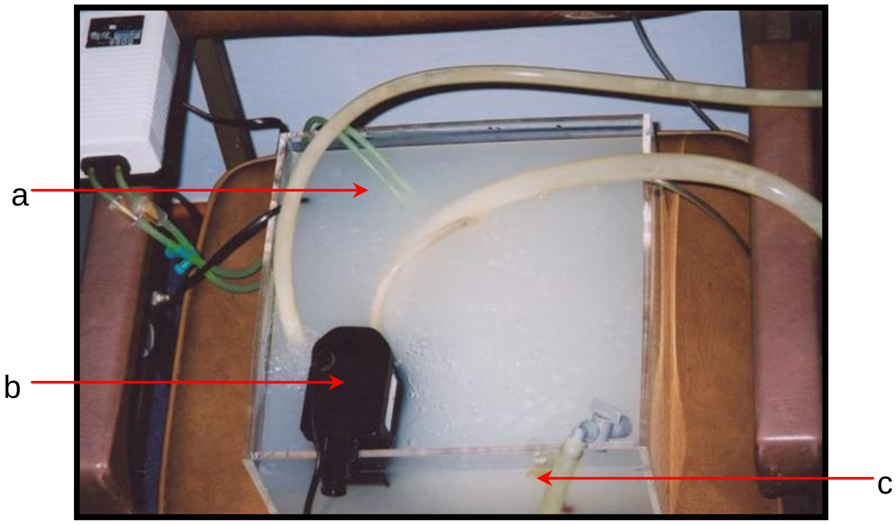


Plate 3.7: The smaller reservoir of the in vitro machine

(a) The smaller reservoir containing Fusayama's artificial saliva, **(b)** Pump re-pumping the artificial saliva, **(c)** Thermometer

3.10 FUSAYAMA'S ARTIFICIAL SALIVA

Although this study did not place much emphasis on the effects of varying pH in saliva, from a physiological perspective, attempts were made such that crucial physical properties on pH were considered to help quantify the composition of Fusayama’s artificial saliva to simulate the conditions in the mouth. The composition of Fusayama’s artificial saliva is detailed in Table 3.3.

Teeth are bathed in saliva and if the pH is not kept sufficiently high they would run the risk of erosion (Oral Environment Online, 2000-10-27). The pH of saliva from resting glands is slightly less than 7.0, but during active secretion the pH level approaches 8.0 (Ganong, 2001: 473). Therefore this study the pH of Fusayama’s artificial saliva was maintained at 8.0, and this value simulates the pH in the mouth.

During the preliminary investigations it was noted that the pH level dropped which was expected and accepted according to literature. Hence, Fusayama’s artificial saliva was produced at a pH level of 8.0, (Department of Biotechnology, Steve Biko Campus, Durban Institute of Technology, Durban, South Africa).

A pH meter (E 520, Metrohm Herisau, Switzerland - Plate 3.8) was used to regularly monitor the pH level in order to avoid an increase in acidity. Replacement of Fusayama’s artificial saliva was performed at the set time periods at 7, 14, 21 and 28 days to avoid saturation of the medium with corrosion products (Barrett et al., 1993). The artificial saliva was not replenished on day 28 when the experiment ended.

Plate 3.8: A pH meter

Table 3.3: Composition of Fusayama's Artificial Saliva

CHEMICAL	FORMULA	QUANTITY
Disodium Sulphide	Na_2S	0.024g
Magnesium Pyrophosphate	$Mg_2 P_2 O_7$	0.024g
Mucin		60g
Urea	$CO(NH_2)_2$	60g
Disodium Hydrogen Phosphate	Na_2HPO_4	9g
Calcium Chloride Anhydrous	$CaCl_2$	9g
Potassium Chloride	KCL	6g
Sodium Chloride	NaCl	6g
Distilled Water		**15 L**

3.11 EXPOSURE CYCLES OF SPECIMENS

To simulate actual conditions in the mouth the sprayed samples were removed from the bath daily for an hour, since it was assumed that exposure to air would stop any crevice corrosion initiated during the wet part of the cycle. At the present time, there is no data available that indicates the optimal time-period required for the specimens to be kept outside the machine in order to prevent crevice corrosion (Hack, 2002).

Gloves were worn at all times during removal of the specimens from the in vitro machine and careful procedures were followed to ensure that the specimens were not touched at the area of the orthodontic SBSS joints.

Galvanic corrosion rates are reliably obtained by direct measurement using zero–resistance ammeters or potentiostats (Pryor & Astley, 1994: v1: 221). However, prevailing time and budget constraints prevented the study from taking this into consideration. In an attempt in ensuring galvanic current rates did not increase radically, the voltage measurement (potential differences) between the orthodontic SBSS specimens in the exposure chamber was monitored and recorded daily with the use of a voltmeter (Leader AC Millivoltmeter - Plate 3.9). Temperature, pH and other important information were also recorded daily (Annexure E).

Initially all 80 specimens (four groups of 20) was sprayed by Fusayama's artificial saliva. After the initial immersion, the first 20 orthodontic SBSS specimens was removed at the set time period of 7 days, followed by the removal of the second, then the third and then the fourth sample groups at the set time periods of 14 days, 21 days and 28 days consecutively.

Samples removed at such time intervals (7, 14, 21 and 28 days) were then subjected to tensile testing. Analysis of the metal elements using scanning electron microscopy and the energy dispersive spectrometry then followed.

The control group was then fabricated and tested after the spray period of the last sample group (28 days), to avoid any bench corrosion (caused by flux salts found on surface of the joint after the brazing procedure) while waiting for the completion of the sprayed sample groups.

Plate 3.9: An AC Millivoltmeter

3.12 TESTING THE SAMPLES

3.12.1TENSILE TESTING OF SAMPLES

Tensile testing of the samples was conducted at the Mechanical Engineering Department, Steve Biko Campus (Durban Institute of Technology, Durban, South Africa) on a LLOYD Tensile Testing Machine

(Model LR 30 K, Lloyd Instruments Ltd., Fareham, Hants, UK – Plate 3.10). As stated previously the sample groups were removed at their specific time periods and tested, finishing with the 28 days sample group and control group.

Plate 3.10 LLOYD Tensile Testing Machine

To avoid torsional forces on the specimens during load, each sample was connected to the machine via axially aligned clamping jigs (Plate 3.2), which were rigidly connected to the fixed (non-moving) base and the load cell on the cross head of the tensile tester. The load cell fitted to the tensile tester had a maximum load capacity of 5000N, with 99.9% calibrated accuracy from 250N through to 5000N. Below this load the accuracy is not guaranteed but is within 5% based on experimentation.

To avoid tearing the specimen at the brazed join, each pair of “wire tags” of each specimen was clamped with care to ensure equal length and thus equal tension distribution. It must be noted that this was done carefully by observation of each specimen under load confirmed that in almost all cases loading was equal on both sides of the brazed joint and tearing effect were minimised.

Each specimen was loaded to fracture point with a fixed rate of separation of 2mm/min. This rate of separation conforms to most metallic specimen tensile testing standards and was chosen here to ensure minimal negative effects on maximum strength due to the rate of strain.

Each specimen was preloaded minimally to ensure that the wire tags did not slip out of the clamping grips and to further avoid the results of static friction between the grips and the specimen prior to proper setting of the specimen in the grip. The preload was removed from the graphical output for ease of understanding, but included in calculations. The specimens were separated and the corresponding load measured. Fracture point in this study was defined as a sudden and significant reduction in load carrying capacity; of which at least 50% of the maximum load achieved in each case.

The maximum load measure was recorded by the software and this was used to determine the ultimate tensile strength for each sample.

3.12.2 NUMBERING AND IDENTIFICATION OF SPECIMENS

The fractured orthodontic SBSS joint specimens for all sample groups were treated in the following manner:

1. The long wire tags or ends were snipped off with a pair of cutting pliers in order to facilitate the:
    i. transport of the fractured orthodontic SBSS joints of the sample groups in a protective plastic box to the SEM unit.

ii. fractured orthodontic SBSS joints to be readily placed on a stub in preparation for scanning electron microscopy and energy dispersive spectroscopy.

Further precautionary measures were taken to ensure that the orthodontic SBSS joints (before and after fracture) were not touched by hand. Failure to comply with this could affect the eventual microscopical and elemental analysis and could contaminate the orthodontic SBSS joints with impurities.

2. The fractured orthodontic SBSS joint specimens for each sample group were placed on a sterile sponge and assigned to a compartment contained in the plastic box (Plate 3.11).

Plate 3.11: Plastic box containing the fractured orthodontic SBSS joints of the sprayed sample groups

For ease of reference the control sample group was kept in a separate box.

3. The sponge for each sample group was numbered 1-20 and was designated with a specific colour, which is as follows:

EXPOSURE PERIOD	*COLOUR*
7 days	**Blue**
14 days	**Red**
21 days	**Green**
28 days	**Black**

The numbering of the individual specimens corresponded to the set of data recorded for each specimen by the LLOYD computerised hardware.

3.13 SEM OBSERVATION AND SURFACE ELEMENTAL ANALYSIS OF SAMPLES

On assumption that orthodontic SBSS specimens experiencing greater corrosion activity produces weaker tensile strengths, five specimens with the weakest tensile strength from each sample set at each experimental period were selected to measure objectively under a scanning electron microscope (Model S-520, Hitachi, Ltd, Tokyo, Japan, Plate 3.12), in order to establish the:

- metal elemental (ions) composition and the surface corrosion properties exhibited by the fractured samples, as determined by energy-dispersive spectroscopy (EDS), under a 20kV accelerating voltage.

- morphological changes of fractured surfaces by micro photographing through the metallographic microscope.

This resulted in a total of 20 specimens available for analysis.

Towards the latter part of this study, a detailed metallurgical study was performed on an orthodontic SBSS specimen. Please note that before elemental analysis, the orthodontic SBSS specimen was embedded in resin, which was ground and polished using standard metallographic techniques and subsequently vacuum-coated with a thin layer of conductive carbon. The brazing zone was studied by means of X-ray mapping under a scanning electron microscope (LEO S440, Germany, Plate 3.13) equipped with energy dispersion spectrometry system (Kevex detector attached to a Sigma computer software) in order to identify the phases, which formed in the solder material.

It must be noted that with energy dispersive spectroscopy (EDS) analysis there are limitations since it involves the detection of x-rays that are emitted as a result of the primary electron beam interaction with the sample (target). Consequently, X-rays are produced from all the elements contained in the volume bombarded by the beam. For example, if one wishes to analyse the composition of the solder metal and there are other deposits present on the surface of the solder (including carbon coating), the EDS system will detect elements present in the solder as well as the elements that comprise the surface deposits. The total element detection is normalised to 100% and therefore the recorded amounts of metallic elements pertaining to the solder are fractions of the total elements detected. In this way, it is not possible to directly compare the elemental values obtained form the EDS spectra, and in some cases the use of element ratios has been preferred (Section 5.3.2).

In addition, the microstructure of the un-etched orthodontic SBSS specimens were further examined under a LEO 1450 (Plate 3.14) and a Phillips XL30 (Plate 3.15) scanning electron microscopes, respectively.

Plate 3.12: Scanning Electron Microscope attached to an EDS System – Hitachi S-520

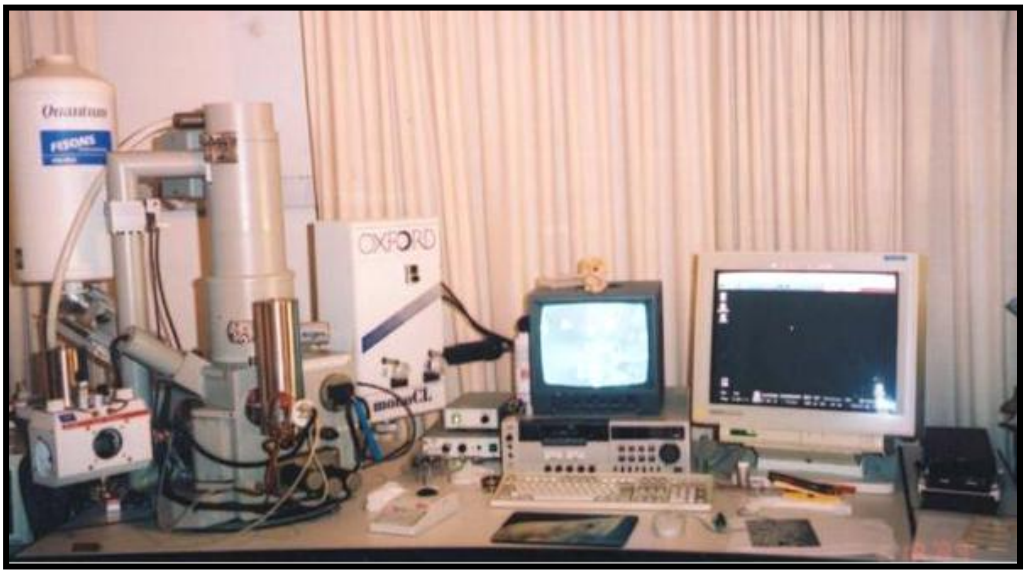


Plate 3.13: Scanning Electron Microscope attached to an EDS System – LEO S440

Plate 3.14: Scanning Electron Microscope - LEO 1450

PLATE 3.15: Scanning Electron Microscope attached to an EDS System – Phillips XL30

3.13.1 ETCHING OF SAMPLES

Orthodontic SBSS joint specimens were etched such that the distinct microstructures were revealed. It was envisaged that the findings of this procedure would influence the evaluation of the corrosion results. Initially, the late Dr F Graham (2003) recommended the random selection and exposure of two fractured brazed specimens from the control sample group to acid etch procedures. The brazed specimens (not mounted in resin) were held by a pair of tweezers and immersed in a solution of 2g $FeCl_3$ and 100mL distilled water for just under a minute (Flowers, 2003). Microscopic analyses then followed.

Towards the latter part of this research the metallurgical complexity of the study had increased and this demanded the implementation of more accurate and precise techniques for reliable and valuable results to be produced. Therefore on recommendation from Prof Robert Knutsen (2004), an orthodontic SBSS specimen from the control sample group was selected and exposed to the proper application of metallographic procedures in preparation for acid etching procedures. The metallographic preparation included:

I. Embedding the orthodontic SBSS specimen in a transparent acrylic hot mounting resin (Struers LaboPRESS-3, Copenhagen, Denmark).

II. Grinding the embedded resin using silicon carbide (SiC) papers, 1200 and 4000 grit (Stuers RotoPol-22, Copenhagen, Denmark).

III. Automatic polishing for 15 minutes with OP-U suspension, high quality colloidal silica of approximately 0.04um, then followed (Struers RotoForce4, MB-NAP automatic polishing pad, Copenhagen, Denmark) until, in cross section, a scratch-free mirror surface of the brazed interface was observed.

IV. Five minutes of ultrasonic cleaning in a water bath finally followed.

The embedded specimen was then immersed in a solution of 2g $FeCl_3$ and 100ml distilled water for 5 seconds, followed by cleaning with Ethanol and water. The embedded orthodontic SBSS specimen was then set for microanalyses.

3.13.2 MICROSTRUCTURAL OBSERVATION UNDER STEREO LIGHT MICROSCOPE

Early in this study quantitative analysis of the sprayed samples groups by SEM/EDS analysis revealed unique surface morphologies. In an attempt to understand and assess if whether a correlation existed between the surface morphologies of the sprayed and unsprayed orthodontic SBSS specimens, a research light microscope (REICHERT MeF3A attached to a LEICA DC 100 computer software program, Austria) was used, prior to and post acid etching procedures, to observe the microstructure of the embedded brazed specimen of the control sample group.

Furthermore, the sprayed orthodontic SBSS joints were also observed under a stereo light microscope (LEICA MZ 8, Austria, Plate 3.16) in order to assess the severity of corrosion with increased exposure time. It was anticipated that the information gained from this technique would have significant application to the findings in this research.

Plate 3.16: Light Microscope, LEICA MZ 8

3.14 ATOMIC ABSORPTION SPECTROMETRY (AA)

Although not part of the initial research planning, concentrations of certain metal elements released in Fusayama's artificial saliva were quantitatively measured by atomic absorption spectrometry, using a Varian Spectra AA20 instrument (Varian Analytical Instruments, Australia –Plate 3.17). This technique is based on the unique spectrum of each element (Barrett et al., 1993).

Plate 3.17: Varian Spectra AA20 Spectrometer

According to Skoog et al. (2000: 626) in AA spectrometry, the sample is converted into an atomic vapour by a process known as atomisation. In this process, the sample is volatised and decomposed to produce atoms and perhaps some ions in the gas phase. It was therefore suggested that this procedure would serve as an important tool in attempting to determine the corrosive nature of Fusayama's artificial saliva.

On the assumption that the extent of corrosion peaked in the last week of testing (28days), producing the weakest orthodontic SBSS joints, a small quantity of Fusayama's artificial saliva was therefore obtained after the last week of testing to quantitatively measure by AA spectrometry, concentrations of Cu, Fe and Ag as detailed in Table 3.4 (Ramnarayan, 2003).

Selection of the three elements for atomic AA spectrometry was based on the following:

- Iron is the main constituent of the parent metal (austenitic stainless steel wire)
- Silver is the main constituent of the filler material (silver solder).
- Copper is the popular element present in corrosion products.

A specific hollow cathode lamp for each element of interest was required. Consequently the technique is extremely expensive. As noted earlier, such procedures were not part of the initial research planning, thus no consideration was given to the costs attached. Nonetheless the procedure was done gratis and this therefore placed the limitation on the number of element concentrations measured. It is assumed that the information gained from this technique would have application to the findings in this research.

Table 3.4: Atomic Absorption (AA) Spectrometry details

AA DETAILS	**ELEMENTS**		
	COPPER ***Cu***	IRON ***Fe***	SILVER ***Ag***
Lamp Current *(milliamperes)*	4.0 mA	5.0 mA	4.0 mA
Fuel	Acetylene	Acetylene	Acetylene
Support	Air	Air	Air
Flame Stoichiometry	Oxidizing	Oxidizing	Oxidizing
Wavelength *(nano meters)*	324.7 nm	248.3 nm	328.1 nm
Slit width (spectral band pass)	0.5 nm	0.2 nm	0.5 nm

3.15 STATISTICAL ANALYSIS

The following statistical tests were applied to address the sub problems:

Sub problem One:

Tensile strengths

A one way analysis of variance for repeated measures was applied to compare the four sample groups obtained at the set time periods of 7days, 14 days, 21 days and 28 days, against the results obtained from the control group.

Sub problem Two:

Metal element (ions) content

A one-way analysis of variance for repeated measures was applied to study the differences on the extent of surface corrosion on metal element (ions) content between the control and each of the four sample groups.

Sub problem Three:

Association between tensile strength and metal element content

Linear Multiple Regression analysis was used to determine if differences existed between the dependent variable, tensile strength, and the independent variables, exposure periods and microstructure.

Level of significance for all test was $\propto = 0.05$ and p – values was used for decision.

CHAPTER FOUR

Probable impossibilities are to be preferred to improbable possibilities.

Aristotle (384-322 B.C)

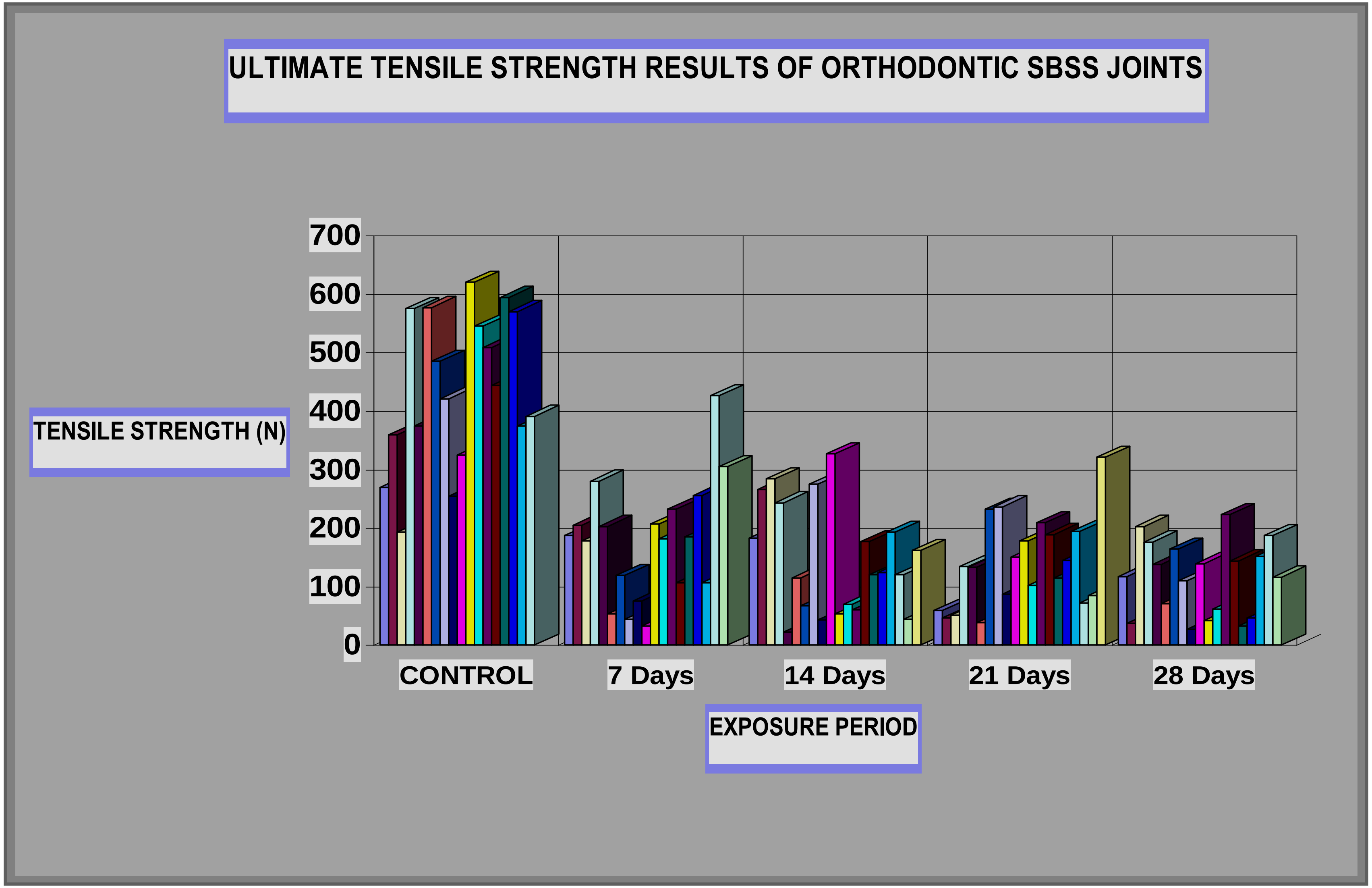
RESULTS

4.1 ULTIMATE TENSILE STRENGTH

The results of the ultimate Tensile strengths for all four-sample groups and the control group, for subproblem one, is summarised in Table 4.1 and illustrated in Graph 4.1 respectively.

Table 4.1: Summary of the ultimate tensile strength results of the sprayed samples groups

SPECIMENS n=20	CONTROL (UNSPRAYED)	REMOVAL TIME PERIOD			
		7 DAYS	14 DAYS	21 DAYS	28 DAYS
1	270	187	183	59	*219
2	359	205	266	46	117
3	193	178	284	51	37
4	575	280	243	134	203
5	375	203	22	133	176
6	577	53	115	38	138
7	485	119	67	232	71
8	421	44	275	236	164
9	255	76	43	87	110
10	*292	33	327	151	27
11	325	207	53	178	139
12	620	182	70	102	42
13	545	232	60	209	62
14	509	107	177	189	223
15	444	185	120	115	144
16	594	256	124	145	33
17	570	107	193	194	46
18	374	426	120	72	152
19	391	305	44	85	187
20	*11.5	*0	162	321	116
MEAN	438	178	147	139	115
***Specimen rejected**					



Graph 4.1: Ultimate tensile strength results of orthodontic SBSS joints

Significant differences were found to exist between the control sample group and the four sprayed sample groups per exposure period at 7, 14, 21 and 28 days (p= 0.00).

Table 4.2 depicts the coefficient of variances between the control sample group and four sprayed sample groups of which all four readings are above 0.10.

Table 4.2: Standard deviations (SD) and coefficient of variances (CV) of the four sprayed and control sample groups

	CONTROL	7 Days	14 Days	21 Days	28 Days
MEAN	438	178	147	139	115
SD	129	99	93	76	62
CV	0.29	0.56	0.63	0.54	0.54

4.2 VISUAL EXAMINATION OF ORTHODONTIC SBSS JOINTS

The nature of the objective results in Table 4.1 and 4.2 and in terms of validity and reliability warranted the subjective examination by visual analysis of the fractured orthodontic SBSS joints in order to help elucidate the corrosion effects on the tensile strength of orthodontic SBSS joints. Visual examination revealed two types of fracture paths as illustrated in Figure 4.1:

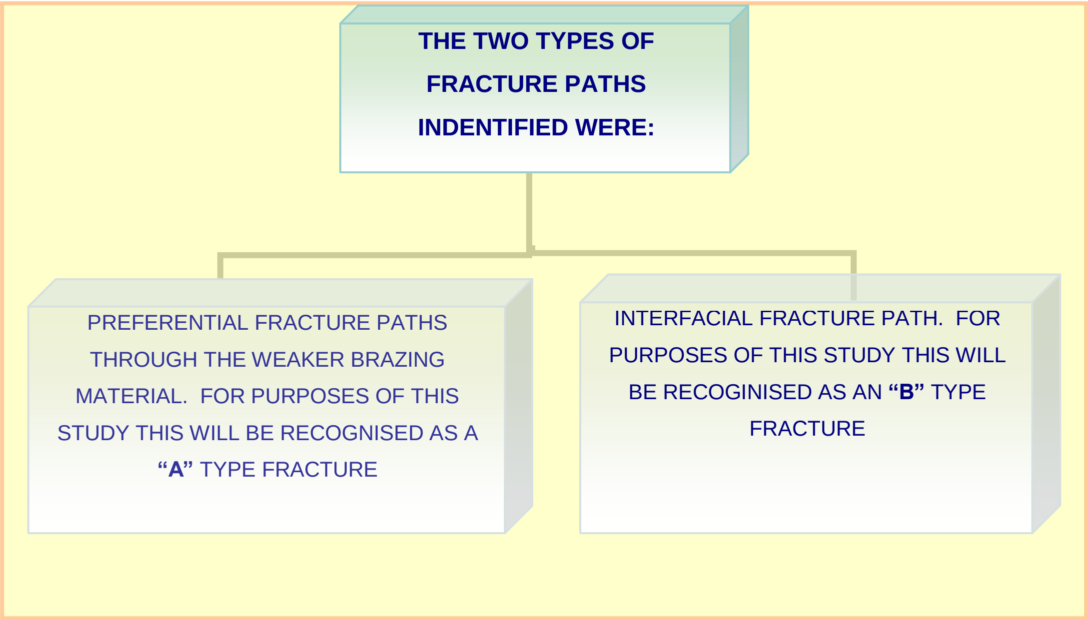
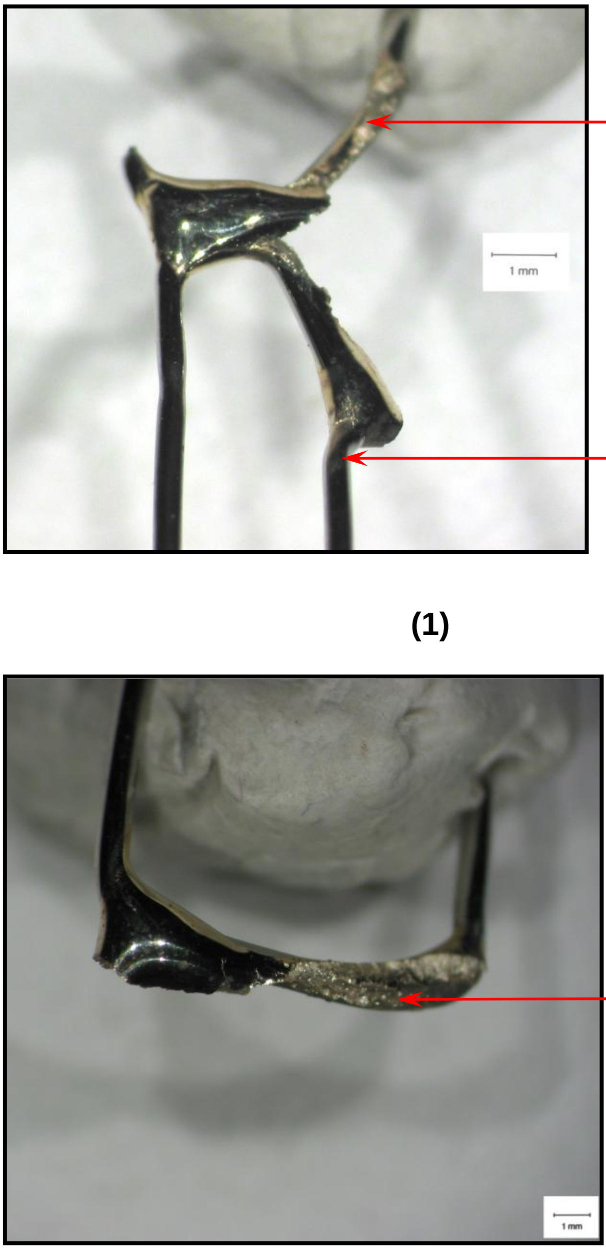


Figure 4.1: Types of fracture paths

The prevalence of these fracture paths in the sample groups is illustrated in Graph 4.2. Results suggest a relationship between fracture path and strength of the orthodontic SBSS joint exists, and is directly related to the exposure period.

4.3 MICROSCOPICAL EXAMINATION OF ORTHODONTIC SBSS JOINT FRACTURES



Wire separates
at the
S/W interface

Wire neck thins
out during
fracture

(1)

“A” type Fracture

(Silver Solder material remains attached to the stainless steel wire surfaces after fracture)

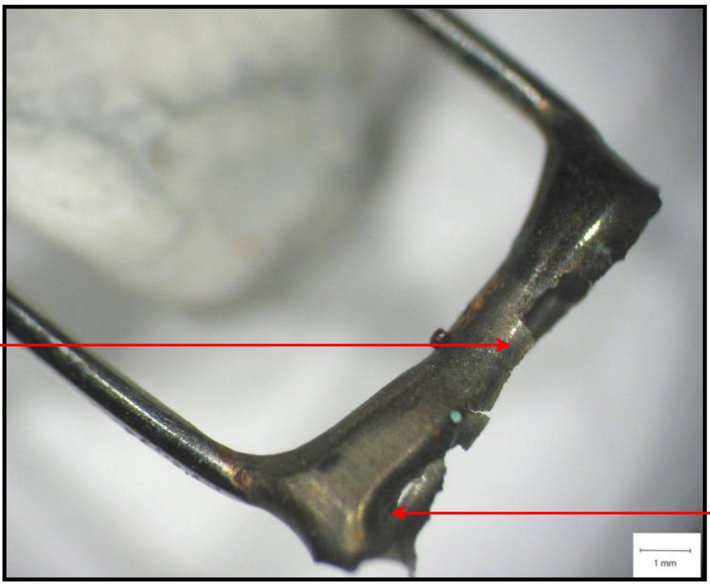
(2)

Plate 4.1: Fractured orthodontic SBSS joints of the control group

1 - Control sample group wire neck thins out and stretches before fracture at the solder/wire **(s/w)** interface

2 - Orthodontics SBSS joints of the control sample group demonstrated “A” – type fractures

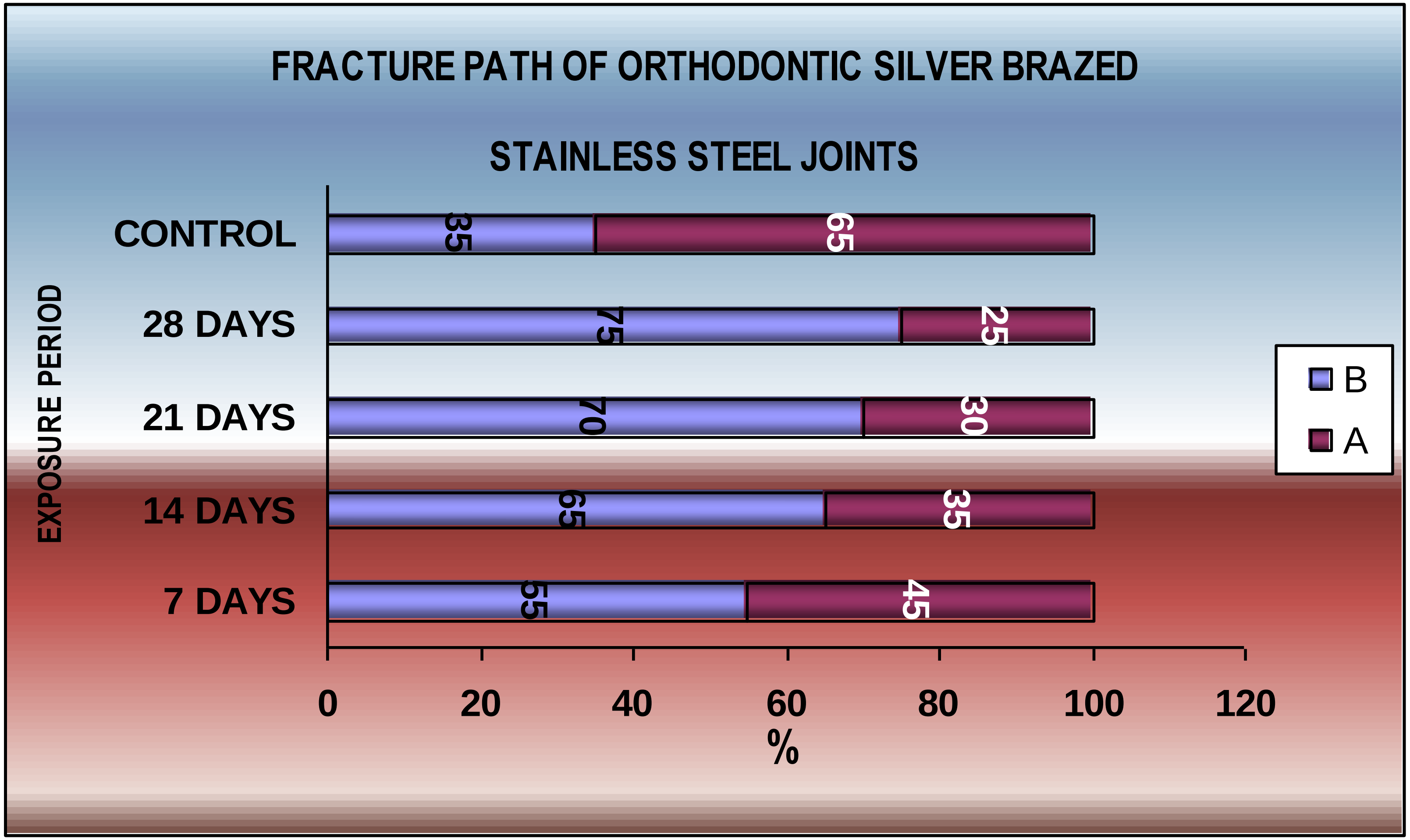
Scale bar = 1 mm



"B" type fracture

Separation at the solder/stainless steel wire interface

Plate 4.2: Orthodontics SBSS joints of the sprayed sample groups demonstrated "B" type fractures without thinning of the wire neck at the s/w interface.
Scale bar = 1 mm



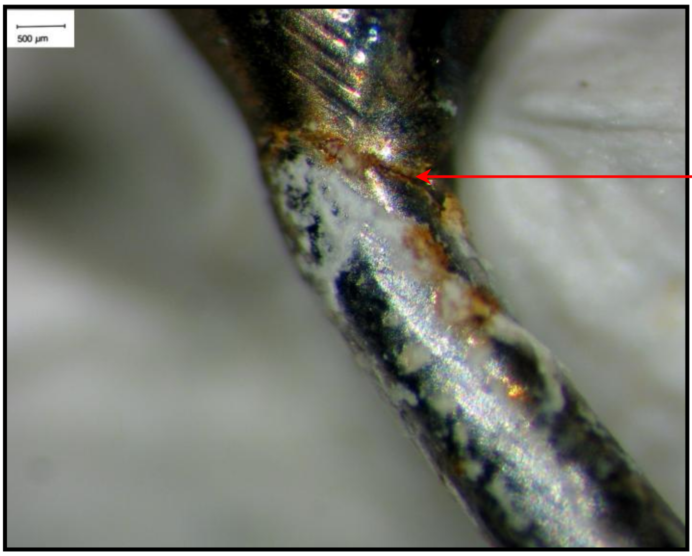
Graph 4.2: Fracture path of orthodontic SBSS joints

4.4 QUANTITATIVE ANALYSIS OF ORTHODONTIC SBSS JOINTS

4.4.1 MACROSCOPICAL ANALYSIS OF THE ORTHODONTIC SBSS JOINTS IN THE IN VITRO MACHINE

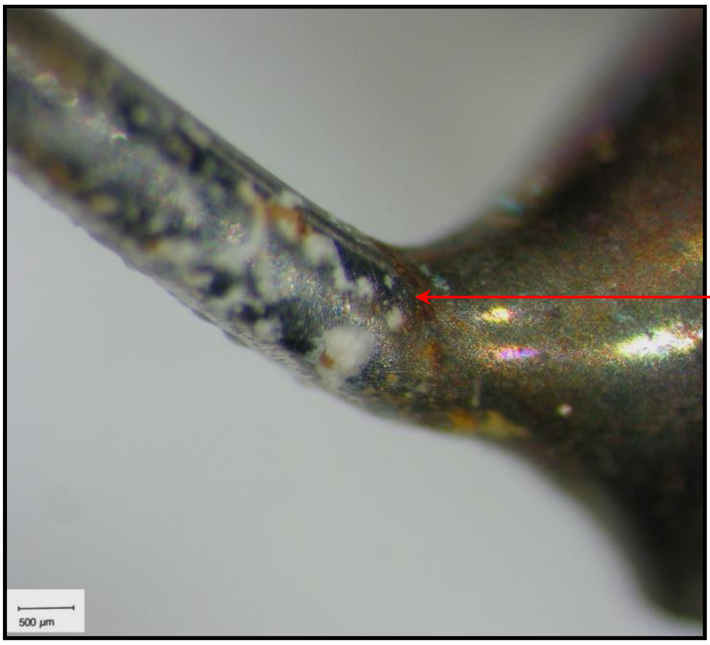
During the first 7 days in the in vitro machine the high surface lustre of the orthodontic SBSS joints tarnished and this markedly increased with longer exposure periods namely at 14, 21 and 28 days. Enhancement of corrosion susceptibility of the orthodontic SBSS joints followed such that rust coloured precipitates manifested at the end of the first exposure period (7 days). Initially, the rust coloured precipitates appeared to be uniformly distributed over the orthodontic SBSS joint surfaces.

However, at the commencement of the 14 days exposure period a more localized form of attack was evident. By the last exposure period at 28 days, the localization of rust coloured precipitates was conspicuously severe at the solder/wire **(S/W)** interface in the area of the tags. This was confirmed by the light microscope results as illustrated in Plates 4.3.



Rust coloured precipitates at the **s/w** interface in the area of the tag

(1)

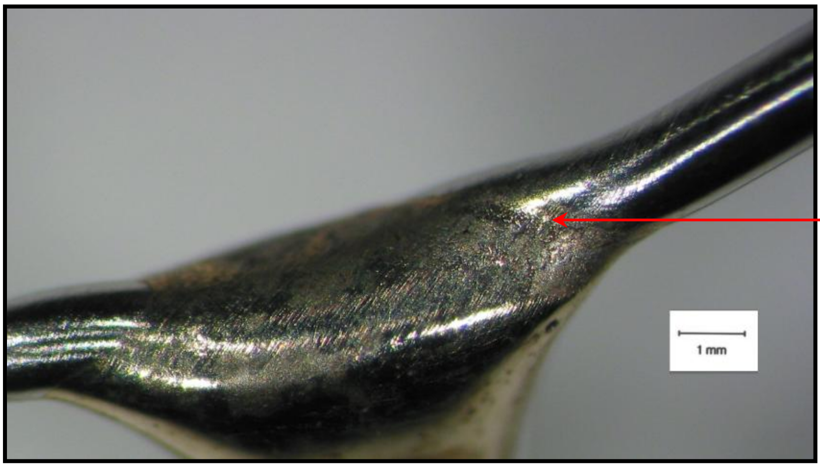


Rust coloured precipitates at the **s/w** interface in the area of the tag

(2)

PLATE 4.3: Light photomicrographs **(1)** and **(2)** highlights the localized rust coloured precipitates at the solder/wire (s/w) interface. Scale bar **(1)** and **(2)** = 500 µm.

In comparison, orthodontic SBSS joints of the control sample group exhibited preserved joint areas between the silver solder material and stainless steel, especially at the s/w interface (Plate 4.4).



Tag area

Plate 4.4: Intact solder/wire (s/w) interface in the Control sample group, particularly at the area of the “tags”. Scale bar = 1mm.

4.4.2 QUANTITATIVE ANALYSIS: ENERGY DISPERSIVE SPECTROSCOPY (EDS) ANALYSIS IN THE SCANNING ELECTRON MICROSCOPE (SEM)

Microscopic analysis of the orthodontic SBSS joints was performed from 3 aspects of which only the main metal element constituents of silver solder and stainless steel were examined, as illustrated in Figure 4.2 below:

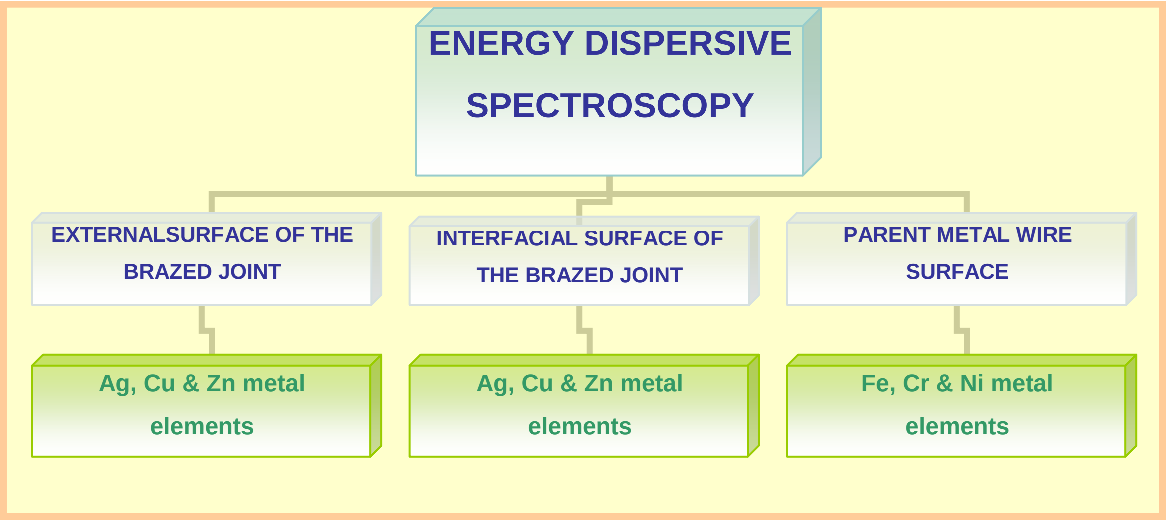


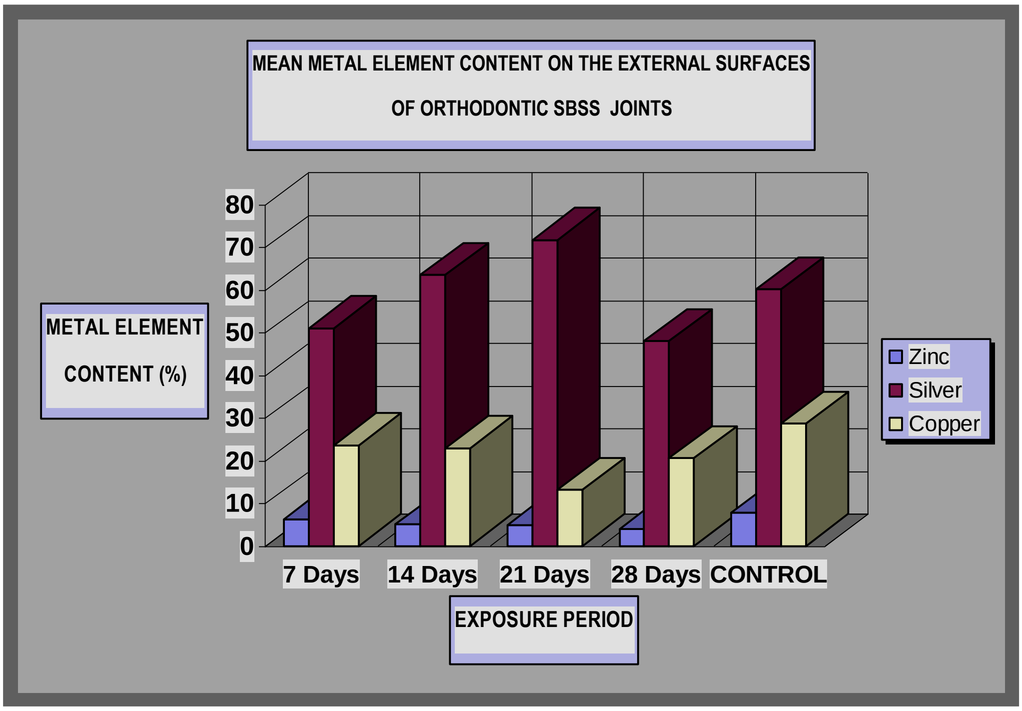
Figure 4.2: Microscopic analysis of orthodontic SBSS joints

The analysis of variance was performed of which the results are summarised in Tables 4.3, 4.4 and 4.5., and is graphically presented in Graphs 4.3, 4.4 and 4.5 respectively.

Table 4.3: Metal element content on the external surfaces of orthodontic SBSS joints

EXPOSURE PERIOD	MEAN			STANDARD DEVIATION		
	Zn	*Ag*	*Cu*	*Zn*	*Ag*	*Cu*
7 Days	6.2	51.0	23.6	3.0	10.4	8.8
14 Days	5.0	63.6	22.9	3.0	10.5	10.0
21 Days	4.9	71.7	13.1	0.8	5.1	2.4
28 Days	4.0	48.0	20.5	0.9	17.7	5.2
Control	7.7	60.1	28.6	0.3	2.5	2.3
Significance	*p=0.07	p=0.01	p=0.02			

*****Not significant at p = 0.05

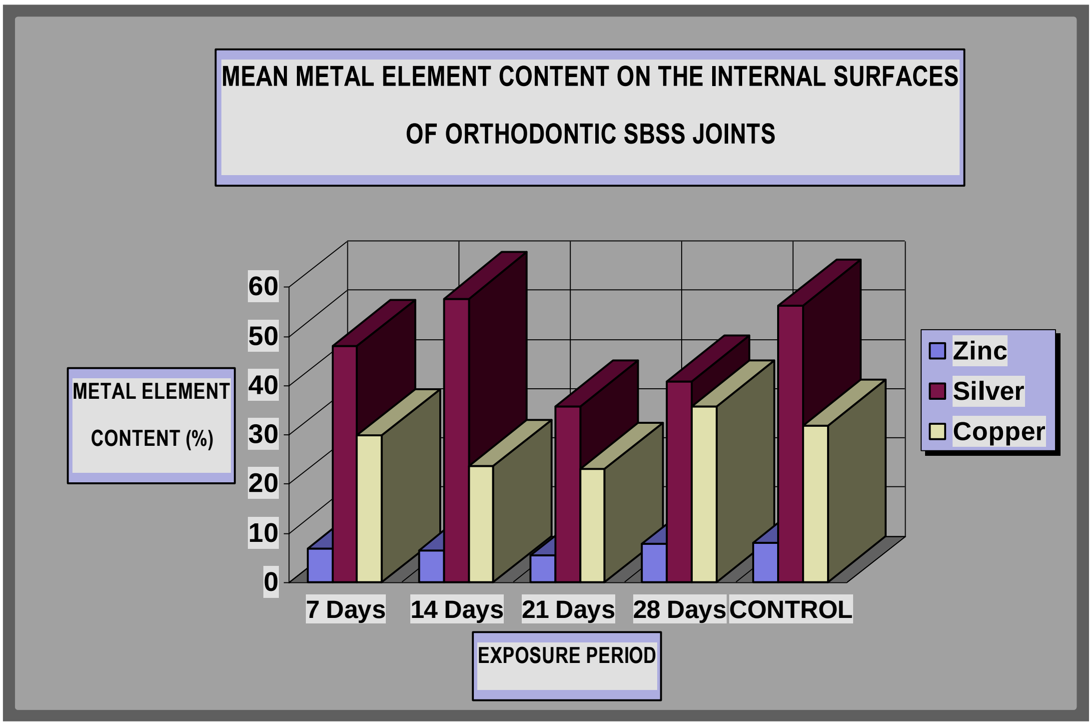


Graph 4.3: Mean metal element content on the external surfaces of the orthodontic SBSS joints

Table 4.4: Metal element content on the interfacial surfaces of orthodontic SBSS joints

EXPOSURE PERIOD	MEAN			STANDARD DEVIATION		
	Zn	***Ag***	***Cu***	***Zn***	***Ag***	***Cu***
7 Days	6.9	48.0	29.8	1.1	6.0	7.0
14 Days	6.5	57.6	23.6	1.0	12.2	4.8
21 Days	5.5	35.7	23.0	2.8	10.2	9.2
28 Days	7.8	40.8	35.7	1.9	21.3	11.9
Control	8.1	56.1	31.7	0.7	5.1	14.1
Significance	*p=0.14	p=0.03	*p=0.07			

*Not significant at p = 0.05

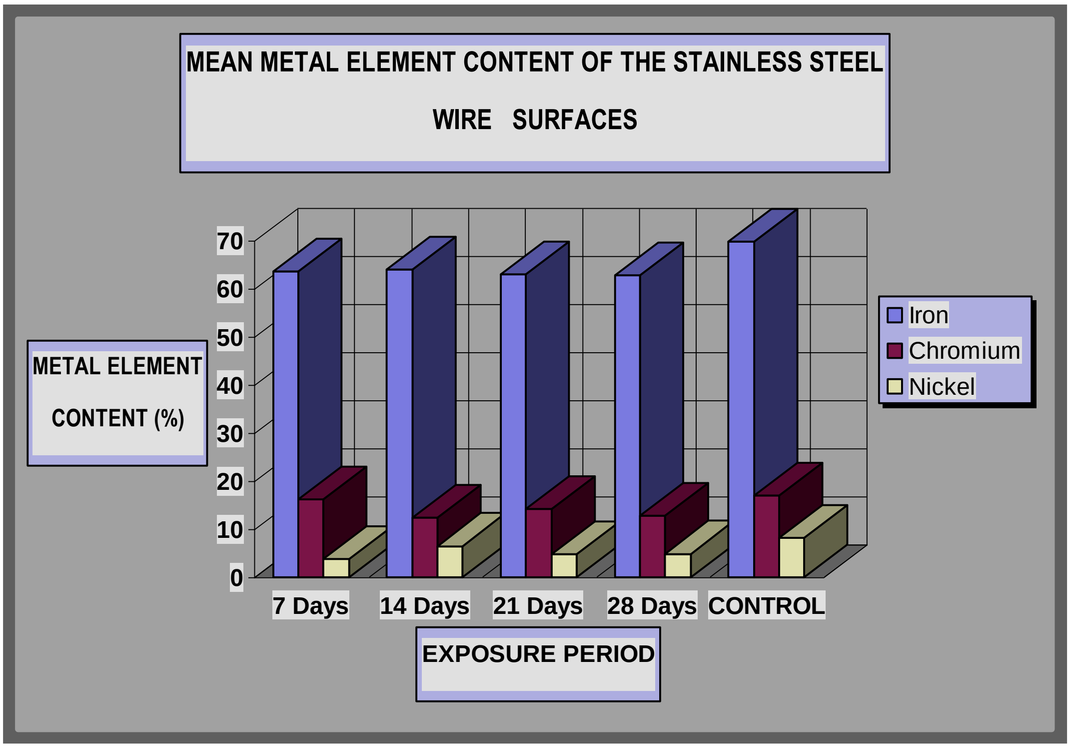


Graph 4.4: Mean metal element content on the interfacial surfaces of the orthodontic SBSS joints

Table 4.5: **Metal element content on the stainless steel wire surfaces**

EXPOSURE PERIOD	MEAN			STANDARD DEVIATION		
	Fe	***Cr***	***Ni***	***Fe***	***Cr***	***Ni***
7 Days	63.6	16.2	3.9	4.8	1.3	3.7
14 Days	64.0	12.4	6.5	10.9	3.0	3.6
21 Days	63.0	14.2	4.8	6.2	2.3	3.3
28 Days	62.8	12.8	4.9	8.5	0.8	3.0
Control	69.7	17.1	8.1	2.6	0.8	0.7
Significance	*p=0.53	*p=0.07	*p=0.24			

*Not significant at p = 0.05



Graph 4.5: **Mean metal element content of the stainless steel wire surface**

4.5 MICROSTRUCTURE AND MORPHOLOGICAL CHARACTERISATION OF ORTHODONTIC SBSS JOINTS

4.5.1 CHARACTERISTICS OF THE SURFACE MICROSTRUCTURE OF THE CONTROL SPECIMENS

I. LIGHT MICROSCOPY RESULTS

Acid etch procedures performed suggested that an association exists between the microstructure specimen of the control sample group (Plate 4.5) and the dendritic/lamellar surface morphology of the sprayed sample groups (Plate 4.8)

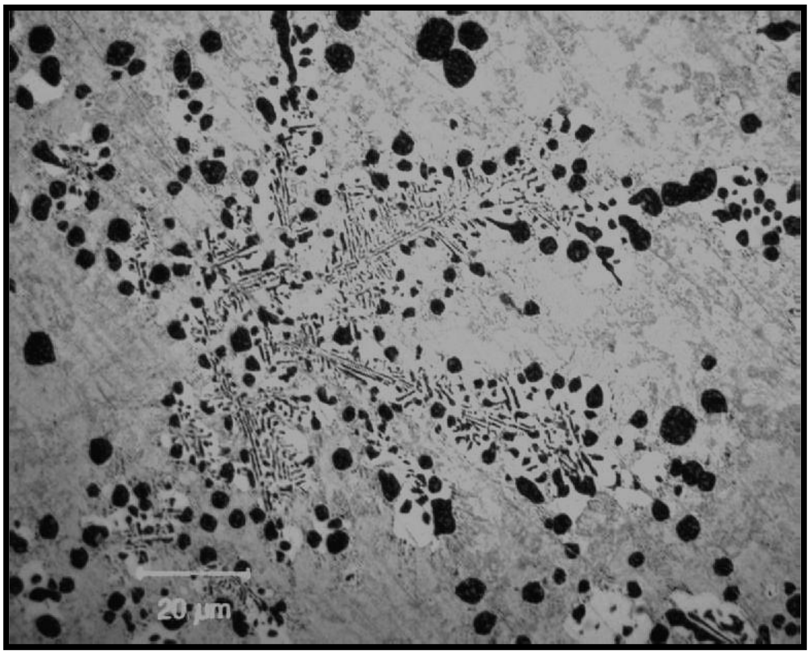


Plate 4.5: Light microscope image of an etched specimen of the Control sample group
Scale bar = 20µm

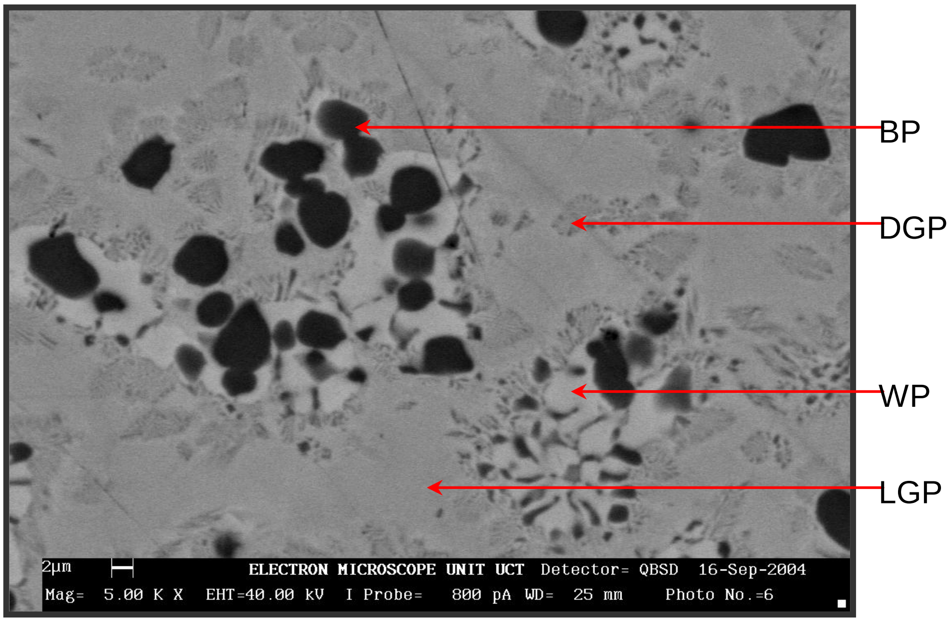
In addition the light microscope results revealed that although a high incidence of Fe precipitates were observed on the wire surfaces, the surfaces of the stainless steel wires (parent metal) were relatively fine.

II. SEM AND EDS ANALYSIS OF THE CONTROL SAMPLE GROUP

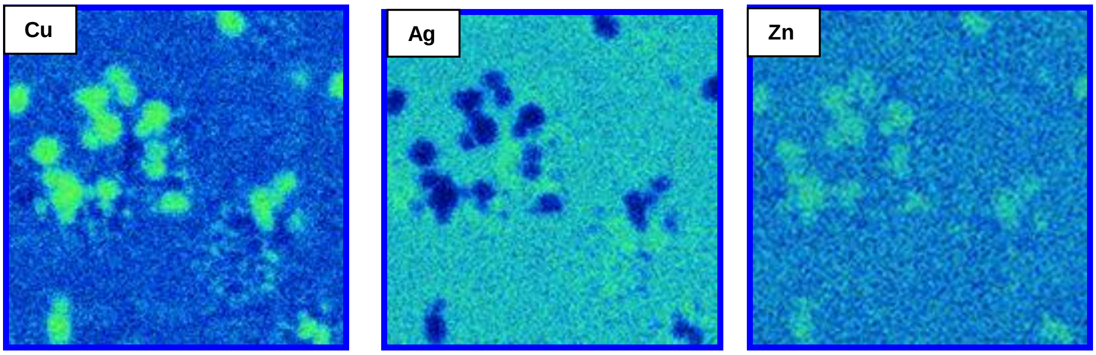
The LEO S440 scanning electron microscope (SEM Unit, UCT, Cape Town) produced back-scattering electron images that revealed the existence of various phases in the silver solder material. In general 4 distinct phases were observed:

1) Grey Phase [Light Grey **{LGP}** and Dark Grey **{DGP}** Phases
2) White Phase **[WP]**
3) Black Phase **[BP]**

The phases formed were analysed using X-ray mapping. The results are presented in Plate 4.6.



(1)



(i) (ii) (iii)

(2)

Plate 4.6: SEM/EDS analysis of an orthodontic SBSS specimen of the Control sample group
(1) Back-scattering electron image of the silver solder material,
(2) X-ray maps of the elements Cu, Ag and Zn
Scale bar **(1)** = 2µm

(Note: blue regions represent low X-ray counts and yellow region represent high X-ray counts.)

The back –scattering electron image and X-ray mapping revealed the following:

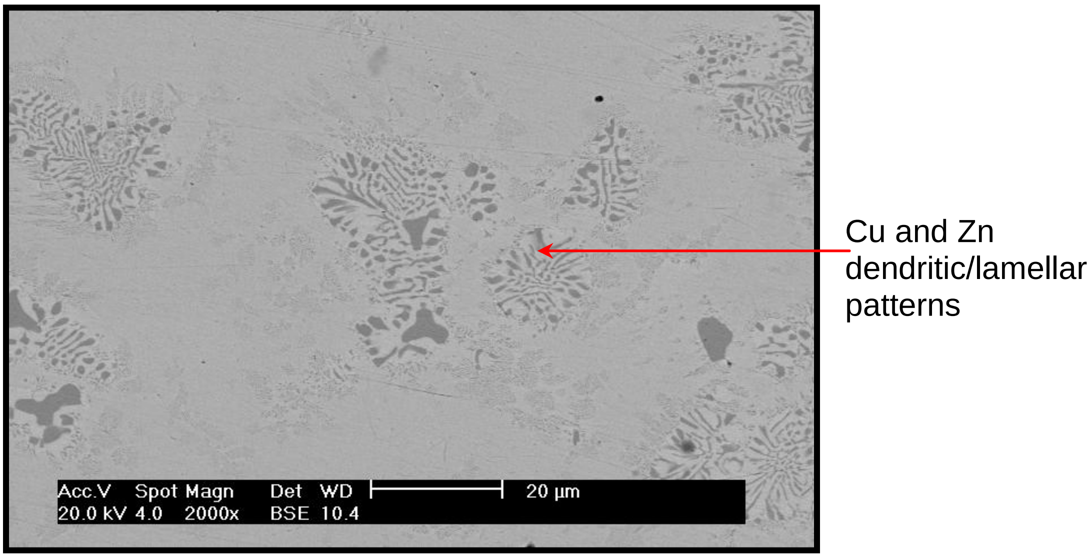
i) Four different phase morphologies existing in the solder material.
ii) The dark phase Cu-rich matrix.
iii) Dominant Ag in both the light and dark grey phases.
iv) Similarity in the distribution pattern of Zn and Cu.

The element composition of each phase as determined by scanning electron microscope and energy dispersal spectroscopy (SEM/EDS) analysis is summarised in Table 4.6 and illustrated in Appendix H, respectively.

Table 4.6: **Element composition (wt %) of orthodontic SBSS joint as determined by SEM/EDS**

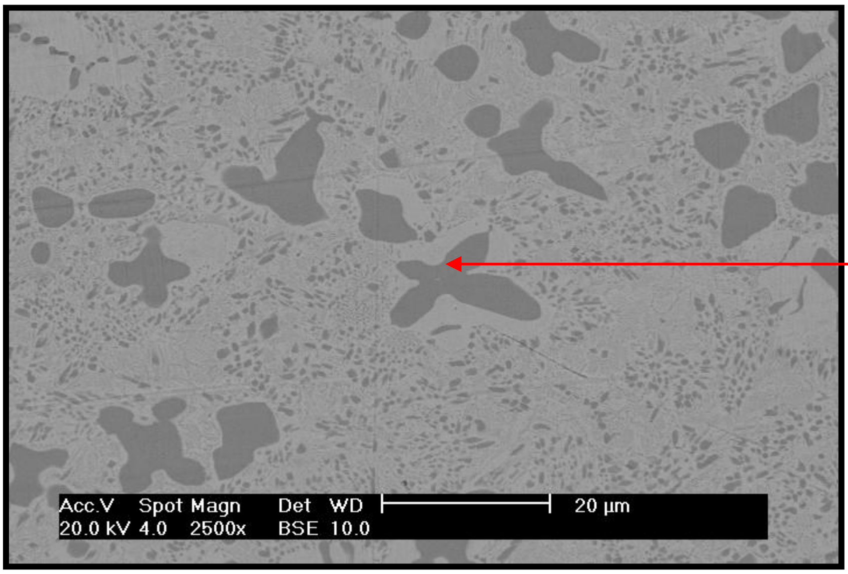
ELEMENTS	DARK GREY PHASE	WHITE PHASE	BLACK PHASE	BULK FROM COMPOSITION (Plate 4.6/1)
Cu	14.04	15.16	49.92	31.86
Ag	73.29	65.30	30.72	44.32
Zn	12.67	19.54	19.36	23.82

The distribution of the dark phase (Cu – Zn rich) is further demonstrated in the electron backscattered image in Plate 4.7/ 1 and 2.



Cu and Zn dendritic/lamellar patterns

(1)



Different phases of the solder material partitioning to star/clover patterns

(2)

Plate 4.7: Distribution of the Cu – Zn rich phase in the orthodontic SBSS joint of the Control sample group

(1) and (2) Dendritic/lamellar and star/clover patterns present on the external surfaces of orthodontic SBSS joints

Scale bars **(1)** and **(2)** = 20µm

4.5.2 EXTERNAL SURFACE MORPHOLOGY OF THE ORTHODONTIC SBSS JOINTS AFTER EXPOSURE IN FUSAYAMA'S ARTIFICIAL SALIVA

Microscopical analysis on the external surfaces of the sprayed sample groups revealed distinctive star/clover and dendritic/lamellae shape patterns that was indicative of the dissolution of the Cu rich and Zn rich phases (Plate 4.8).

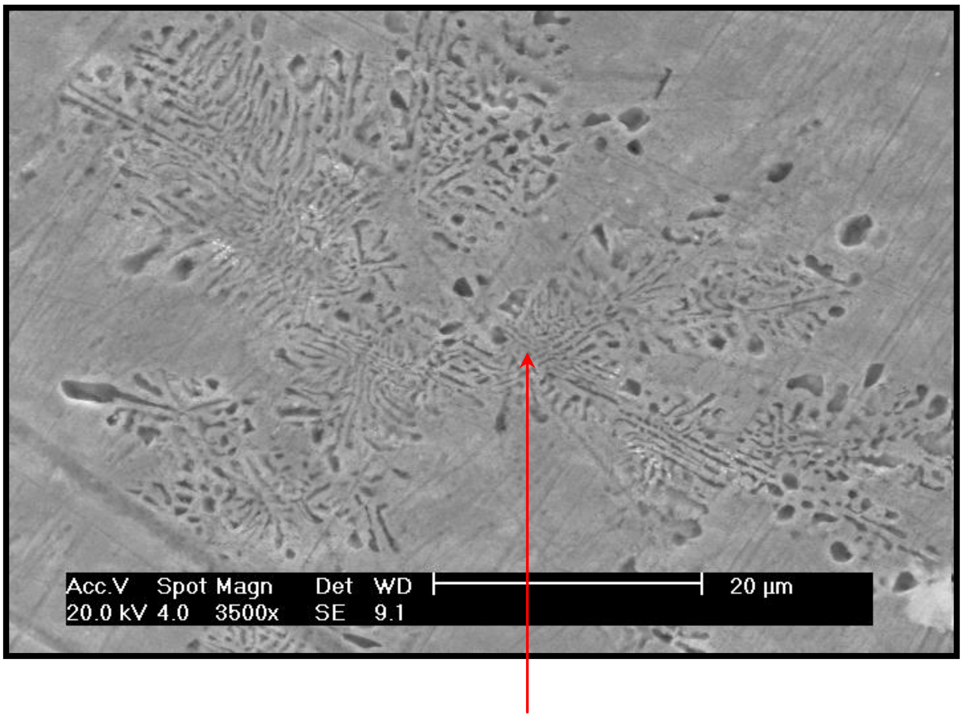
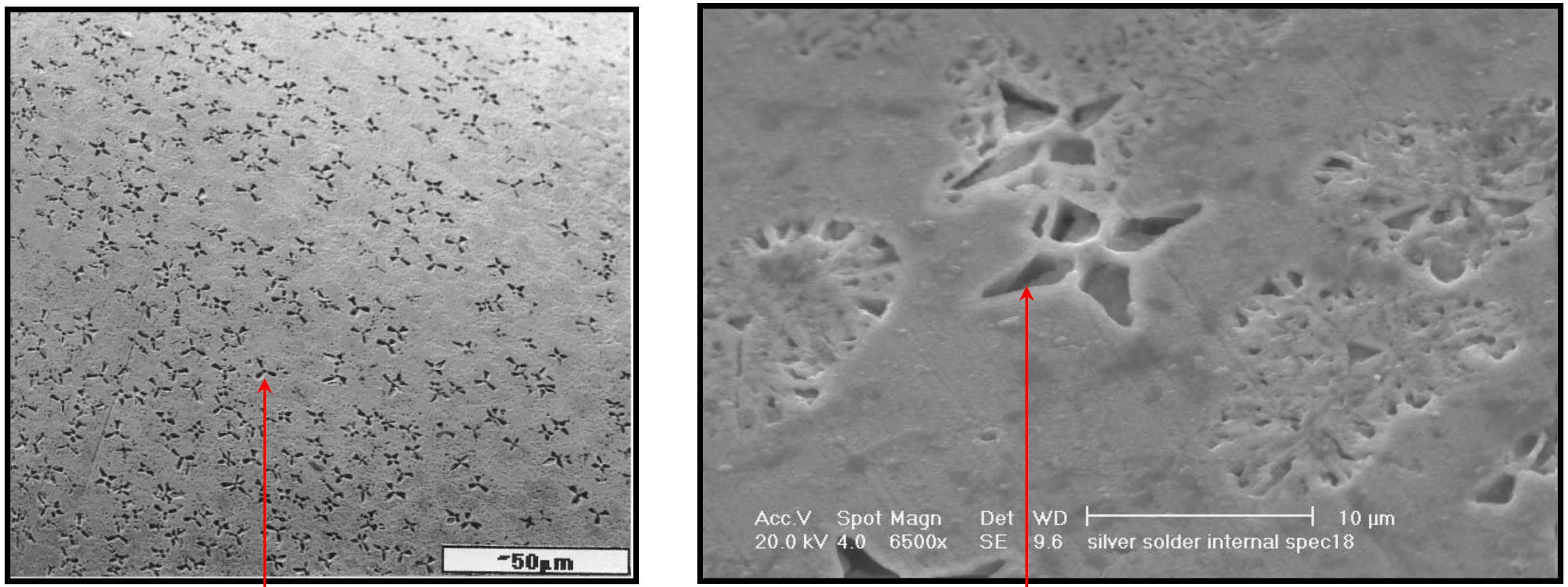


Plate 4.8/ 1: Dendritic/lamellae patterns

Scale bar = 20µm



(2) Star/clover patterns on the external surfaces of the SBSS joints under low magnification

(3) Concave star/clover patterns under higher magnification

Plate 4.8: SEM photomicrographs of the external surface morphology of orthodontic SBSS joints after exposure to Fusayama’s artificial saliva

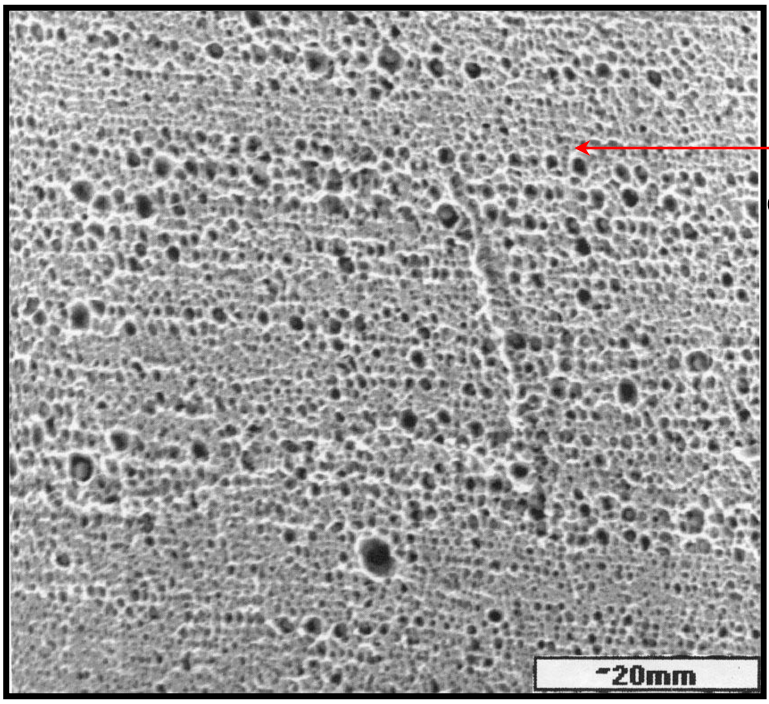
(1) Highlights dendritic/lamella patterns present on the external surfaces of the brazed joints;

(2) and (3): Star/clover patterns present on the external surfaces of the brazed joints.

Scale bars **(1)** = 20µm, **(2)** = 50µm and **(3)** = 10µm

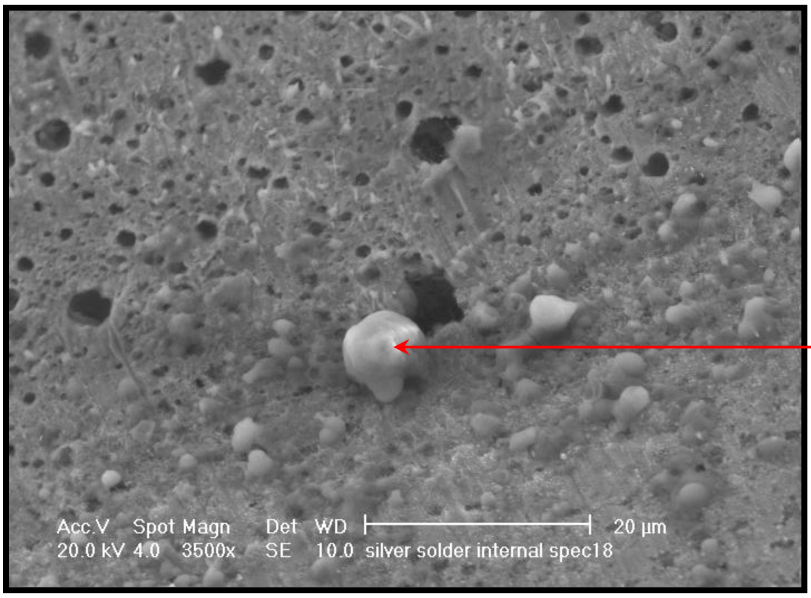
4.5.3 COMPARISON OF THE SURFACE MORPHOLOGY OF THE ORTHODONTIC SBSS JOINTS INTERFACIAL SURFACES BEFORE AND AFTER EXPOSURE IN FUSAYAMA'S ARTIFICIAL SALIVA

Microscopical analysis revealed that the interfacial surfaces of the orthodontic SBSS joints of the control and sprayed samples groups were porous. However, interfacial surfaces of the orthodontic SBSS joints of the sprayed sample groups further revealed the presence of corrosion precipitates (Plate 4.9).



Interfacial porous surfaces of the orthodontic SBSS joints of the Control sample group

(1)



Precipitate at the interfacial surfaces of orthodontic SBSS joints of the Sprayed sample groups

(2)

Plate 4.9: SEM photomicrographs of the interfacial surface morphology of the orthodontic SBSS joint highlighting the:

(1) Porous nature of the brazing material interfacially;

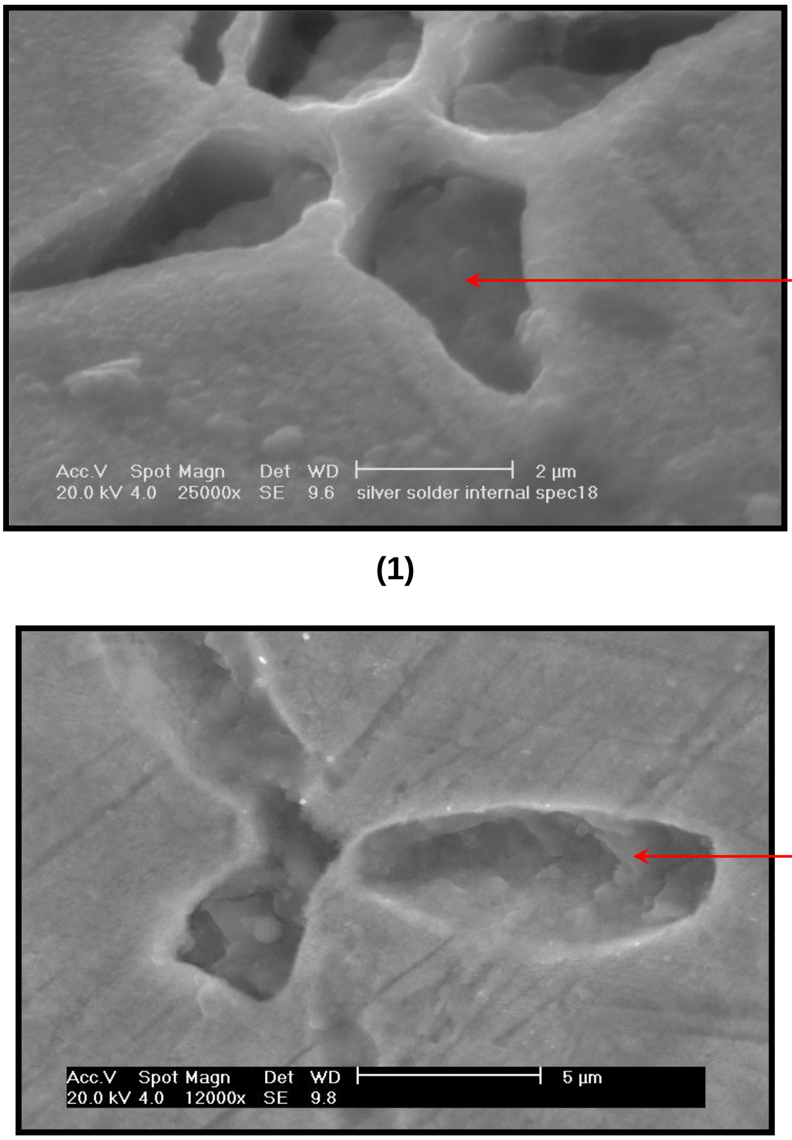
(2) Precipitates at the interfacial surfaces of the Sprayed sample groups

Scale bars **(1)** = 20mm and **(2)** = 20µm

4.6 ASSOCIATION BETWEEN TENSILE STRENGTH, MICROSTRUCTURAL FEATURES AND EXPOSURE PERIOD

4.6.1 QUALITATIVE ANALYSIS

The longer the exposure to Fusayama's artificial saliva, the greater the concavity of the star/clover patterns on the external surface of the orthodontic SBSS joints (Plate 4.10).



Increase concavity of pattern with increased exposure time

(1)

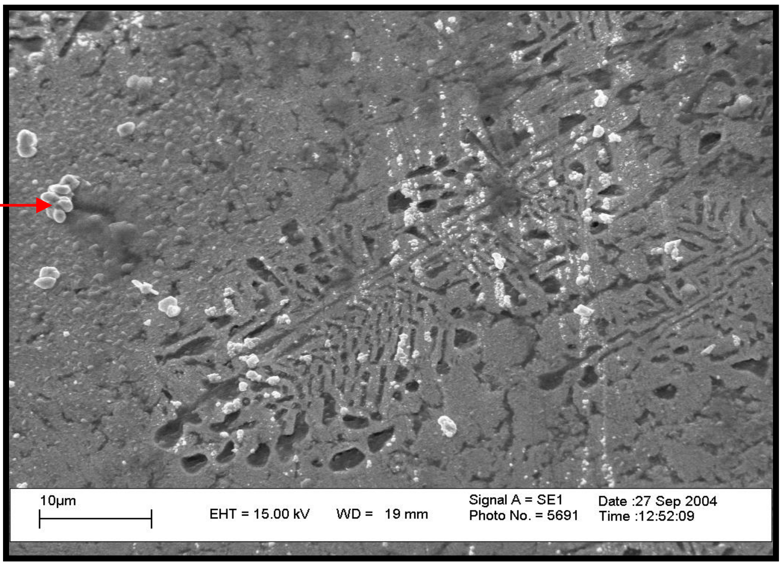
Higher magnification revealing concave star/clover patterns

(2)

Plate 4.10: **(1)** and **(2)** Concave star/clover patterns of the Sprayed sample groups

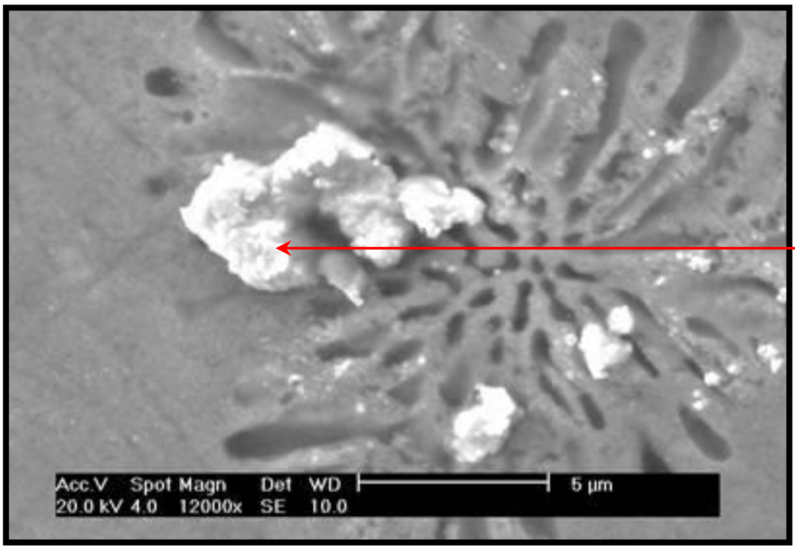
Scale bars **(1)** = 2µm and **(2)** = 5µm

Along with the patterns, precipitates were also present on the external surfaces of the orthodontic SBSS joints of the sprayed sample group (Plate 4.11).



The presence of various crystalline precipitates on the external surfaces of the orthodontic SBSS joints

(1)



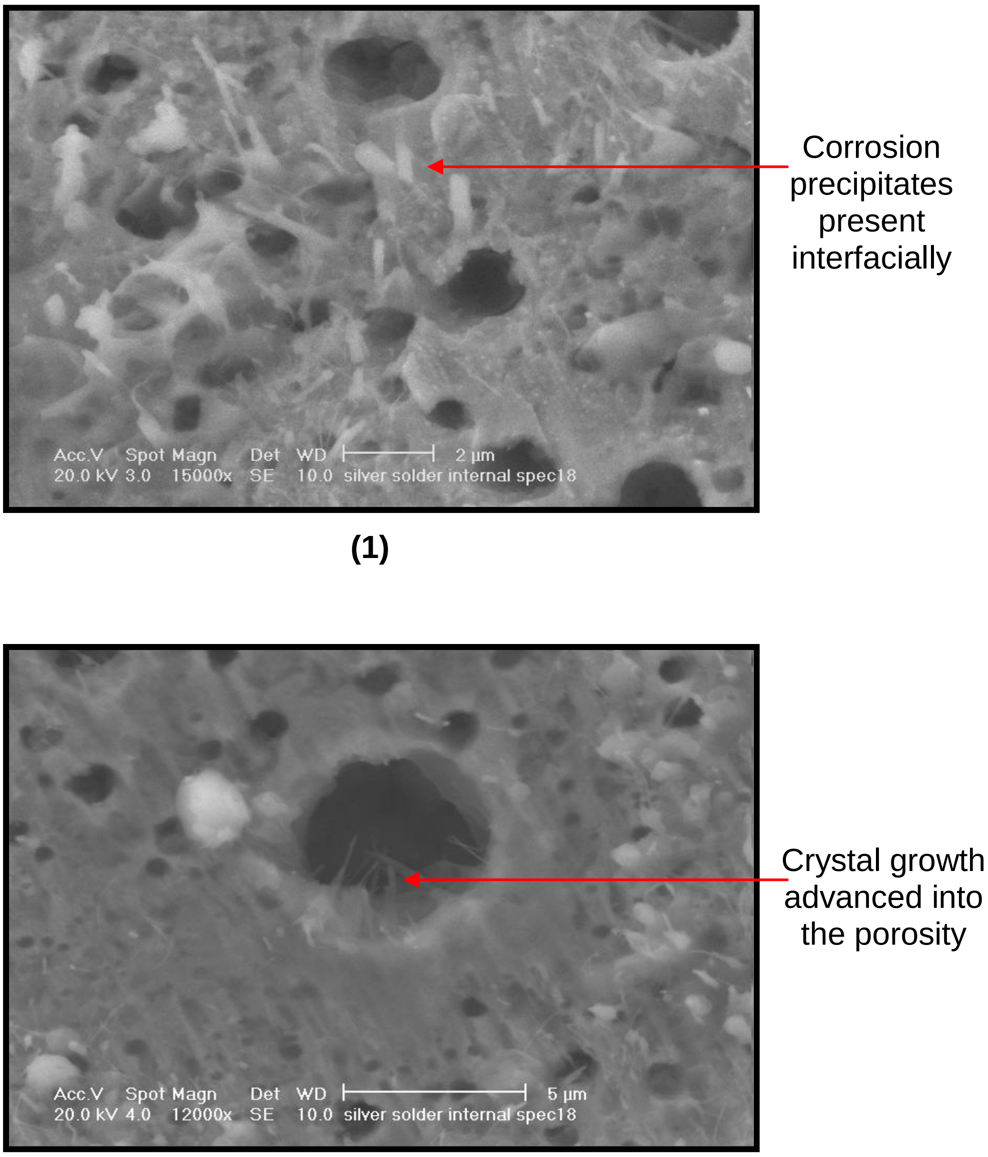
Precipitates on the external surfaces of the orthodontic SBSS joints under higher magnification

(2)

Plate 4.11: **(1)** and **(2)** External microstructure of orthodontic SBSS joints of the Sprayed sample groups revealing dendritic patterns with the presence of corrosion precipitates

Scale bars **(1)** = 10µm and **(2)** = 5µm

Interfacially, prolong exposure exacerbated the presence of corrosion precipitates such that precipitates progressed into the porosities of the silver solder brazing material (Plate 4.12).



(1)

(2)

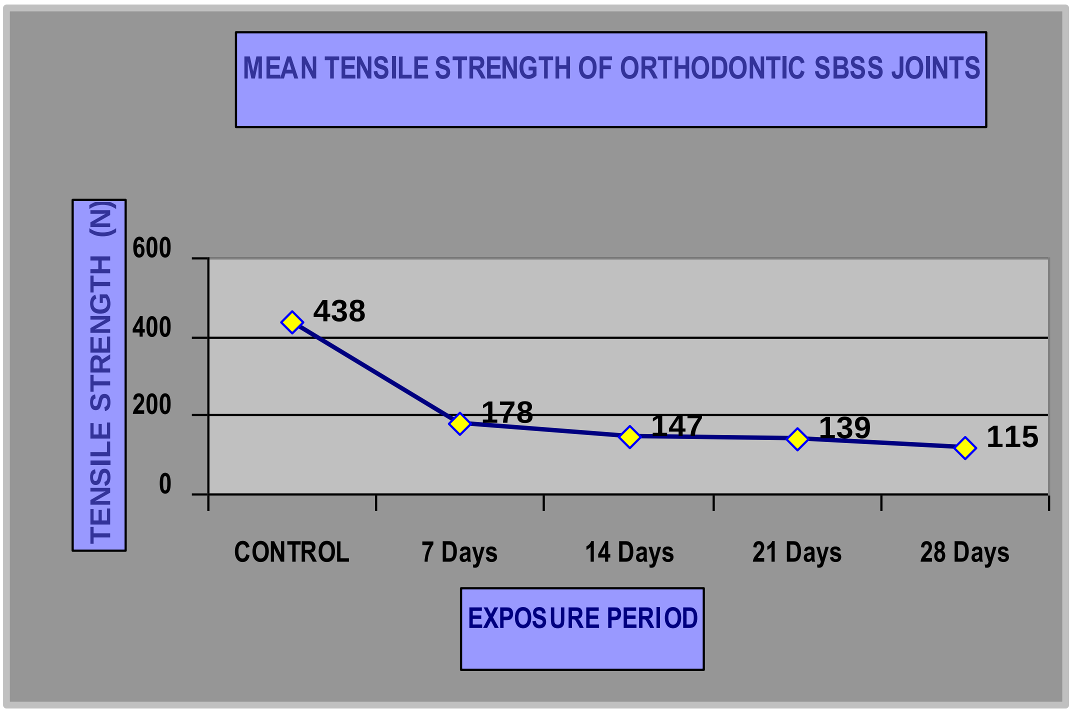
Plate 4.12: Interfacial surfaces of orthodontic SBSS joints of the Sprayed samples groups

(1) Presence of precipitates in the interfacial surface of the silver solder brazing material

(2) Crystals advanced into the porosities of the silver solder brazing material

Scale bars **(1)** = 2µm and **(2)** = 5µm

Furthermore, in comparison to the control sample group externally and interfacially the microstructural and morphological characteristics of the orthodontic SBSS joints consequently influenced the reduced tensile strengths of the sprayed sample groups per exposure period (Graph 4.6).



Graph 4.6: Mean tensile strength of orthodontic SBSS joints

In light of the above, prolong exposure produces a marked decline in tensile strengths of orthodontic SBSS joints of the sprayed sample groups, confirming that a direct relationship exists between the microstructure of orthodontic SBSS joints and exposure period.

4.6.2 STATISTICAL ANALYSIS

The elemental analysis data of the primary elements present on the external, interfacial and parent metal wire surfaces (Tables 4.3, 4.4 and 4.5) was used to determine and evaluate the relationship between the tensile strengths, exposure period and microstructure of the fractured orthodontic SBSS joints of the sprayed sample groups. Statistically the regression analysis used revealed that no significant difference existed in terms of confirming that a correlation existed between exposure period and microstructure and their combined effects thereof on the tensile strengths of orthodontic SBSS joints (Figure 4.3).

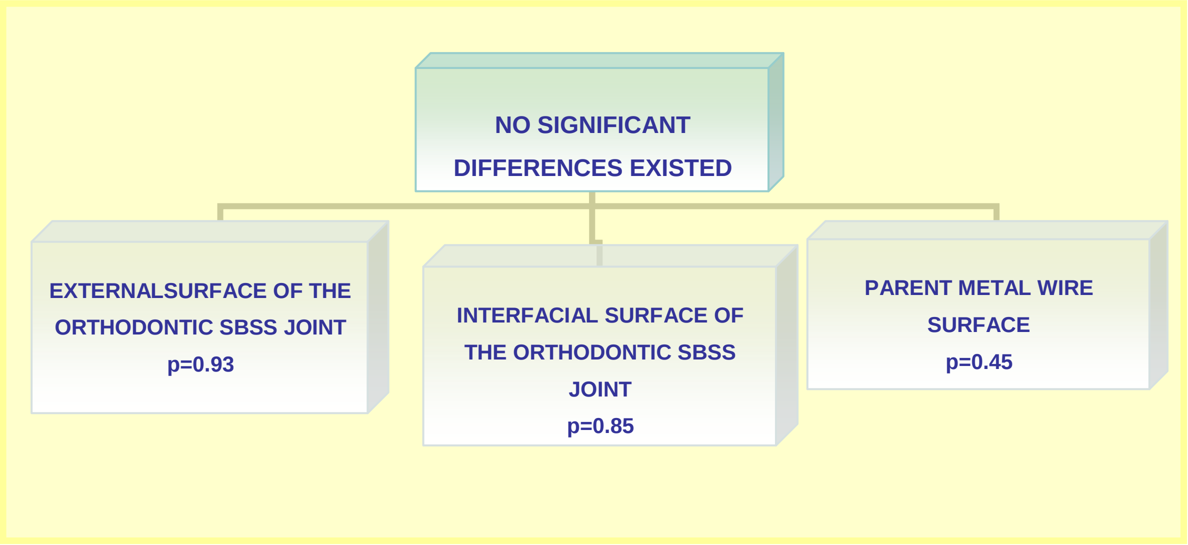
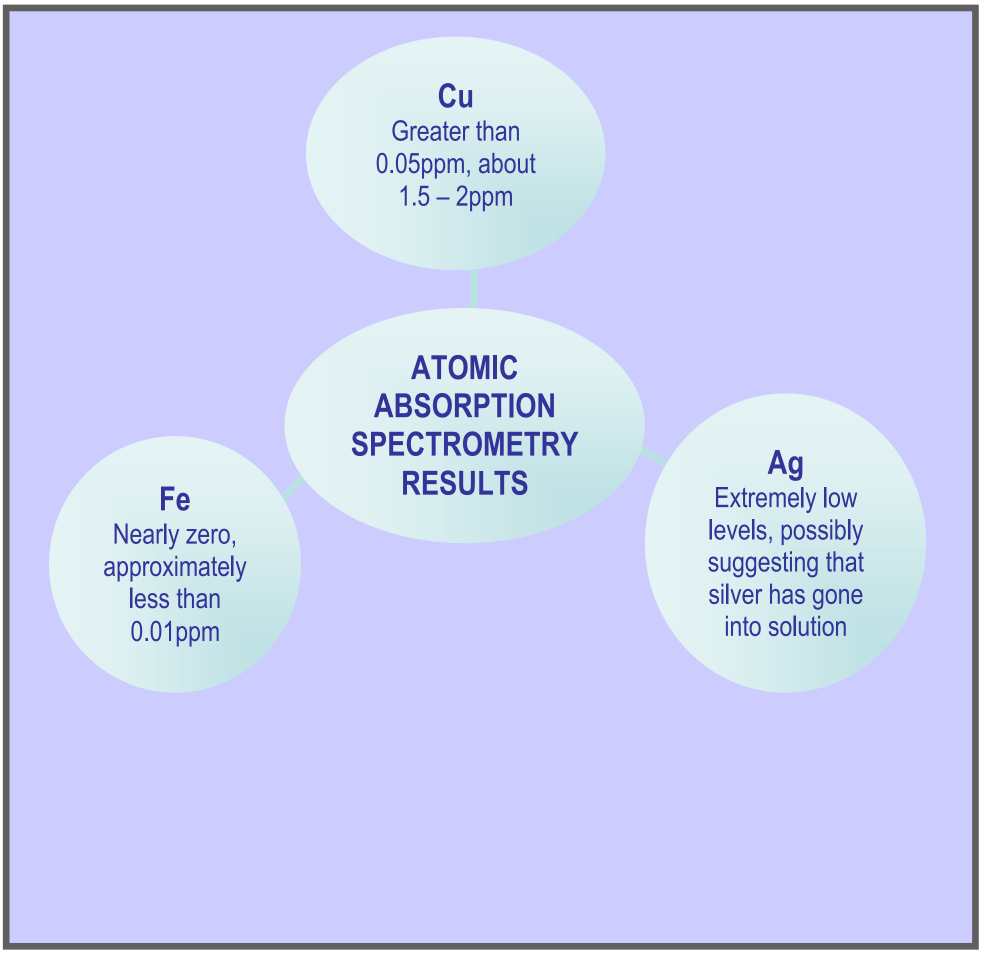


Figure 4.3: The statistical regression analysis of the primary elements of orthodontic SBSS joints from the various surfaces

4.7 ATOMIC ABSORPTION SPECTROMETRY (AA) OF FUSAYAMA'S ARTIFICIAL SALIVA AFTER EXPOSURE

After the 28 day exposure period, AA spectrometry was performed on Fusayama's artificial saliva. It was acknowledged that Cu was not present in the electrolyte prior to spraying the orthodontic SBSS joints. Furthermore, the performance of AA spectrometry simply served to support the findings of the results that Cu dissolution of the silver solder brazing material occurred, which enhanced the concavity of the star/clover morphological patterns on the external surfaces of the orthodontic SBSS joints (plate 4.8).



Ag
Extremely low levels, possibly suggesting that silver has gone into solution

Figure 4.4: Atomic Absorption spectrometry results of Fusayama's Artificial Saliva after exposure

CHAPTER FIVE

Discovery consists in seeing what everyone else has seen and thinking what no one else has thought

Albert Szent-Gyorgi (1937)

DISCUSSION

5.1 INTRODUCTION

The clinical performance of silver solder brazing materials, employed in the construction of orthodontic appliances, significantly depends on the mechanical properties of the brazed combination and its resistance to degradation to the varying environmental conditions of the mouth. An increase in the observed deterioration of orthodontic appliance, containing SBSS joints, has therefore influenced the design of this in vitro study to address and establish the relationship between the microstructure of orthodontic SBSS joints and the effects of corrosion on these joints by objectively measuring the tensile strengths from varying exposure periods in Fusayama's artificial saliva.

In general, the main findings of this study were that the tensile strengths of orthodontic SBSS joints reflected significant difference as a function of exposure time when analysed statistically. The microstructure of such joints was identified as a source for selective corrosion, particularly when exposed to a wet environment, where the propensity for corrosion appreciably enhances.

5.2 SUBPROBLEM ONE - ULTIMATE TENSILE STRENGTH

Although certain specimens were rejected due to errors in the setting of the testing machine, this had no significant effects on the overall results. Statistical analysis was able to draw correlation between measure tensile strengths and exposure period. This is manifest by the fact that the p-value, which “in hypothesis testing is the exact probability of obtaining, when the null hypothesis is true, a value of the test statistic as extreme as or more extreme (in the appropriate direction) than the one actually computed” (Thomas, 2001: 24), was less than 0.05 (Appendix I). The mean tensile strengths produced by the sprayed samples groups were also below the mean of the control sample group (Section 4.1 - Table 4.1).

Previous investigators have observed that the strength of brazed joints is dependent on several factors, including the strength of the metals to be joined, flux inclusions and voids, gap distances between the parent metal surfaces, type of brazing techniques employed and corrosion resistance (Laird and von Fraunhofer, 1972; Rasmussen et al., 1979; O’ Toole et al., 1985; Angelini et al., 1991, Gawlik et al., 1996 and Heidemann et al., 2002). Nevertheless, these studies failed to reveal the combined influence of the metallurgy, intra-oral exposure period and corrosion on the tensile strength of orthodontic SBSS joints, of which this study has focussed.

When brazing stainless steel wires with silver solder in the fabrication of orthodontic appliances, it is imperative that the wires be completely covered by the solder material as this enhances bond strength by producing a stronger joint. Although this study delimited the effects of the brazing technique employed, it must be taken into consideration that orthodontic brazing by torch flame soldering has proven to produce stronger joints (O’Toole et al., 1985 and Gawlik et al., 1996), and that temperature variations during brazing inevitably exist (Tehini and Stein, 1993). Therefore it is unrealistic to expect precise control from even a skilled technician when torch flame soldering procedures are employed for brazing.

With regards to the brazing temperatures employed, this study further corroborates the findings of Berge et al., (1982), Brockhurst and Pham, (1989) and Gjerdet and Hero (1987) to the extent to which it confirms prolonged heating in the temperature range of 620°C to 665°C or above, is critical, as the integrity of the orthodontic SBSS joints inevitably diminishes. This "technique" related problem, which at times is beyond the control of the operator, appears and poses to be an influential contributor to the low reproducibility of uniform orthodontic SBSS joints.

In addition, the longer the exposure to any physiological saline environment, the greater is the potential weakening in the tensile strengths of orthodontic SBSS joints. Results of this study therefore demonstrated that the hypothesised decline in the mean tensile strengths per exposure period of the four sprayed sample groups existed, consecutively at 7, 14, 21 and 28 days. However, statistically the degree of skewness reflected was much more than twice its standard error between the control sample group and sprayed sample groups (Appendix I), indicating that a wide range, along with the difficulty in producing consistent results exist when orthodontic SBSS joints are concerned. The degree of skewness reflected in the results further validated the use of non-parametric testing (Kruskal Wallis - Appendix I). Both parametric (*ANOVA*) and non-parametric tests revealed similar results, p=0.00. It is therefore postulated that the one-month exposure period employed for this in vitro study proved to be substantially short as the difficulty in producing uniform joints accounted for the degree of skewness thereby producing broad differences in the co-efficient of variances and standard deviations (Section 4.1 – Table 4.2).

In reviewing the literature, Phillips (1991: 543) states that, "although an intimate contact between the metals is seen, present evidence indicates that no measurable amount of atomic diffusion occurs at the interface and that the bond is strictly mechanical". This study is in agreement that no alloying existed at the solder/wire **(s/w)** interface and confirms the presence of a mechanical bond. This is consistent with other studies performed by Gawlik et al., (1996) and Rogers (1979).

The theory of orthodontic SBSS joints possessing a purely mechanical bond between the metals is further supported by the different fracture paths observed between the control sample group and the sprayed sample groups. The control sample group revealed “A” type fractures and the sprayed samples groups demonstrated “B” type fractures (Section 4.2 – Figure 4.1 & Graph 4.2). The apparent “A” type fractures demonstrated by the control sample group is largely due to the joints not being exposed to a wet environment within which the susceptibility of the joints to corrosion is enhanced. Furthermore, the absence of such an environment, allows the solder material bulk around the parent metal wire surfaces to be retained. In agreement with O’ Toole et al., (1985), this results in the wire neck thinning out as it stretches during fracture and separates at the interface (Section 4.3 - Plate 4.1/1).

According to O’ Toole et al., (1985), the greater mass of solder around the parent wires undoubtedly constitutes a more intense heat source at the s/w interface than with the uncovered wire. This greater heat may possibly produce a more extensive and different mode of solidification of both the parent wire surfaces and silver solder brazing material. This study fully emphasized that such differences positively affected the metallurgical characteristics, and more importantly the strength of orthodontic SBSS joints.

The “B” type fractures evident in the sprayed sample groups were positively influenced by longer exposure periods that encouraged a more localized attack, especially at the S/W interface (Section 4.3. – Plate 4.2). In addition, “B” type fractures suggested that the bond strength of the silver solder brazing material to the stainless steel parent wire surfaces after exposure was less than the strength of the solder itself (Laird and von Frauhofer, 1972).

The differences in the path of fracture between the control sample group and the sprayed sample groups is therefore directly related to the distribution of corrosion products especially at the s/w interface or at other localized areas of the orthodontic SBSS joints. In agreement with Angelini et al., (1991), corrosion products when present at an interface may thus cause substantial decrease in the strength of the brazed joint.

Statistically, this study produced significant differences between the sprayed sample groups and control sample group. The hypothesis for subproblem one, that the orthodontic SBSS joints exposed to Fusayama's artificial saliva will produce different levels of predictability and tensile strengths to the control, and will thereby set parameters for comparison, was therefore accepted.

An important point that needs to be highlighted, that it is also critical to consider the value of qualitative analysis in assessing the outcomes of this research. Therefore, in deliberation of the qualitative examination, the nature of the brazing technique and time of exposure are possibly determining factors on the tensile strengths of orthodontic SBSS joints. Furthermore, the decrease in tensile strength with prolonged exposure time further suggests that the corrosion resistance of orthodontic SBSS joints presents an ongoing problem.

5.3 SUBPROBLEM TWO - MICROSTRUCTURE OF ORTHODONTIC SBSS JOINTS

The investigation of the microstructure of orthodontic SBSS joints was designed to employ a quantitative measurement tool to relate the extent of corrosion to the metal element content on the surfaces (both external and interfacial). This was not possible due to the presence of precipitates on the surfaces after exposure that led to "contamination" of the EDS analysis. A qualitative tool was therefore employed that analysed the differences in microstructure between the control and sprayed sample groups.

Similarly, the light microscope data confirmed that the quality of the orthodontic SBSS joints at the solder/ wire **(s/w)** interface of the sprayed sample groups was severely compromised as opposed to the control sample group. A discussion on the reasons for accepting the validity of these findings follows:

5.3.1 STATISTICAL ANALYSIS ON THE METAL ELEMENT CONTENT

After exposure to Fusayama's artificial saliva, SEM/EDS analysis was performed over a broad area of the orthodontic SBSS joints on the external and interfacial surfaces of the silver solder brazing material and the stainless steel parent wire surfaces. In terms of reflecting reliable results, this statistical analysis, as previously mentioned in Section 3.13, was not accepted as results were influenced by the presence of diluted precipitates. This is confirmed by the analytical results of the primary alloying elements of the silver solder brazing material (external and interfacial surfaces) and the stainless steel parent wires which do not equate to 100% as highlighted in Appendix F.

The analytical results of the metal element content were influenced by other elements, which was indicative of the presence of diluted precipitates. Although the results from the statistical analysis are not viable, it has been included in this section in order to emphasise the importance of SEM and EDS analysis as a determinant of reliable results.

5.3.2 CHARACTERISATION OF THE MICROSTRUCTURE OF ORTHODONTIC SBSS JOINTS

According to von Fraunhofer (1997), the microstructure of a metal is a basic parameter that affects both its mechanical properties and in particular, its corrosion behaviour. This study clearly emphasized that the microstructure of orthodontic SBSS joints present vulnerable sites for corrosion that is continually exacerbated by the galvanic action between dissimilar metals. Moreover, when such orthodontic SBSS joints are exposed to a conducting electrolyte such as Fusayama's artificial saliva the tendency towards corrosion is appreciably enhanced, thereby significantly influencing changes in microstructure. This compares favourably with several other studies on corrosion by Berge et al., (1982), Mueller (1981), Gjerdet and Hero (1987), Platt et al., (1997), Kim and Johnson, (1999) and Kusy (2000).

Macroscopic corrosion evident on the surfaces of the orthodontic SBSS joints was characterised by increased surface roughness along with the deposition of corrosion products, which corroborates with the findings of von Frauhofer, (1997). It is interesting to note that the silver solder brazing material in itself deteriorated due to microscopic corrosion and in this rests the concern. Therefore, the complex microscopic corrosion within the silver solder brazing material has set forth the possible theories which will be detailed further.

Brazing around 620°C to 665°C with subsequent quenching decreases corrosion resistance. EDS analysis confirmed that upon solidification, more than 8% of copper was present and this encouraged the appearance of the characteristic lamellar black and white eutectic phase regions (Anusavice, 1996: 339). Copper is the common active element in the corrosion process and has a reactive role in the galvanic couple of orthodontic SBSS joints by producing the progressive dissolution of the less noble dental alloy when coupled to stainless steel, thereby inducing adverse biological effects over prolonged intra-oral exposure periods. This corroborates with past studies by Bayramoglu et al., (2000) and Zinelis et al., (2004).

It must be considered however, that although this study was not initially aimed at performing acid etch procedures, its efficacy nonetheless proved to be instrumental in disclosing a possible association between the surface morphology of the sprayed sample groups (Plate 4.8/1) and the etched microstructure specimen of the control (unsprayed) sample group (Plate 4.5).

The applied metallographic procedures after being subjected to acid etching revealed the topographical features that control the properties and performances of the metal. Four phases within the brazing solder material were revealed and are shown to contain differing elemental composition. It is therefore postulated that the segregation of the elements to the four different phases during non-equilibrium solidification influenced the morphology of the solidification structure and in particular the patterns of the dendritic/lamellar structures. In this way the complicated microstructure/composition distribution of the silver solder has exacerbated the galvanic effect between the dental alloy and stainless steel.

However, when orthodontic SBSS joints were exposed to a wet environment such as in Fusayama’s artificial saliva for long periods, the corrosion tendency of orthodontic SBSS joints was potentiated (Angelini et al., 1991 and Shin et al., 2003). Subsequently, corrosion by selective dissolution of the Cu-rich and Zn-rich phases transpired, producing concave star/clover patterns (Plate 4.8/2 and 3) as opposed to the previously smooth patterns (Plate 4.7/1 and 2).

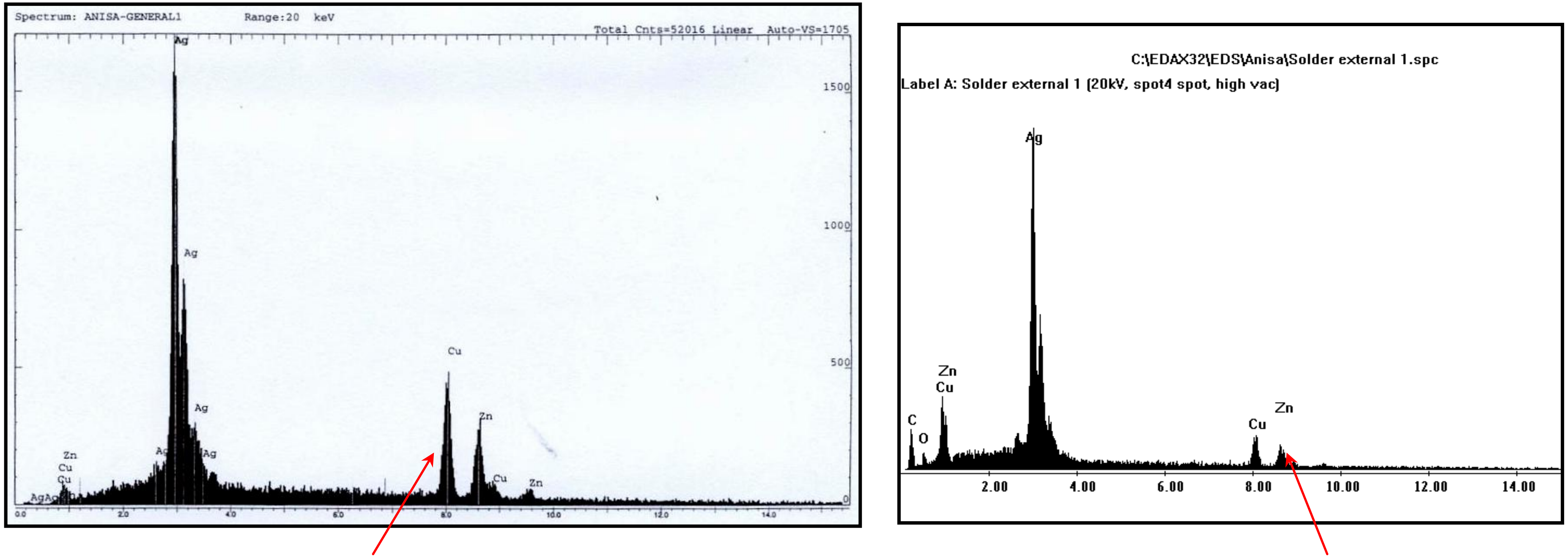
Such proliferated patterns increased in concavity with prolonged exposure time (Plate 4.10/1 and 2). The results demonstrated that due to the particular solidification mode, an intense interconnected network between the dark Cu-rich phase and Ag-rich phase (white phase) occurred that allowed for the selected corrosion process to penetrate deep into the bulk silver solder material. This compares differently to the study by Mueller (1981) who observed that selected corrosion processes occurring within silver solders does not proceed deep into the bulk material.

SEM/EDS analysis further revealed and confirmed the selective dissolution of the silver solder material. A noticeable decline in the Cu: Zn and Zn: Sn ratios between the control sample group and the sprayed sampled groups were identified. Correspondingly, an increase in the Ag: Cu ratio was observed (Table 5.1). The spectral illustrations (Plate 5.1) further validate the declining Cu and Zn peaks when compared to the height of the Ag peak. It should be noted that with spectral analysis there is always the incidence of other elements to be present and in order to negate this incidence, ratios of the primary silver solder constituents were used to observe the changing relationships between Ag, Cu and Zn elemental levels.

In reviewing the literature it was suggested that silver solders are similar in behaviour to that of eutectic alloys and the cooling procedures applied in the brazing procedures influence the solidification process. This in turn significantly influences the morphology of orthodontic SBSS joints. As it is beyond the scope of this study, it is therefore recommended that any future research work on orthodontic SBSS joints evaluate the effects of cooling rates in order to characterise the development of the new phases in the solidified system (Zinelis, 2004) and their effects thereof on the strength and microstructure of the joint.

Table 5.1: EDS Ratio Results

RATIO	CONTROL	SPRAYED
Cu: Zn	1.34	1.25
Ag: Cu	1.39	5.15
Zn: Sn	3.94	2.40



SEM/EDS analysis of the external surfaces of the Control Sample Group

SEM/EDS analysis of the external surfaces of the Sprayed Sample Group

Plate 5.1: EDS revealed decreasing levels of Cu and Zn on the external surfaces of orthodontic SBSS joints of the sprayed sample group when compared to the control group

5.3.3 THE INFLUENCE OF EXPOSURE TIME ON CORROSION AND MORPHOLOGICAL CHANGES OF ORTHODONTIC SBSS JOINTS

5.3.3.1 External Surface of Orthodontic SBSS Joints

Given that silver solder dissolves microgalvanically, macrogalvanic corrosion between the stainless steel and silver solder at the area of tags favours increased corrosion. This allows the electrolyte to corrode this area until such time microcracks develop (Plate 4.3). This favours and enhances electrolyte percolation and concurs with the notion of “precrack electrolyte entering” a system (Knutsen, 2004).

The light microscopic results in section 4.4.1 (Plate 4.3) visibly affirmed that increased exposure time produces small cracks at the s/w interface, especially in the area of the tag, favouring electrolyte percolation. This further facilitated intense corrosion localization, increased crack propagation at the s/w interface and gross deterioration of the silver solder material around the wire. Decohesion of the silver solder from the stainless steel wire eventually resulted. This negatively influenced the overall mechanical and physical properties of the orthodontic SBSS joints. In comparison, the control sample group notably demonstrated intact orthodontic SBSS joints especially at the areas of the tags (Plate 4.4) and the silver solder material bulk enclosure of the parent wire metal surfaces was conspicuous.

Selective dissolution of the Cu and Zn led to the formation of crystalline corrosion precipitates that appeared to be clustered on the surfaces of the orthodontic SBSS joints (Plate 4.11). Iron was also detected in some of the precipitates and is most likely to have occurred by at least some dissolution of the wire. There was also a high incidence of Cl and Ca crystalline corrosion precipitates on the external surfaces of the orthodontic SBSS joints that co-precipitated with Cu, Zn and Fe. This reinforces that the degree of galvanic corrosion phenomena was compounded by the electrochemical nature of Fusayama's artificial saliva.

It should be noted, that no attempt was made to remove and examine these corrosion precipitates, other than that microscopically analysed on the orthodontic SBSS joints. The high incidence of precipitates, particularly Cl, indicates that the passive oxide layer of the orthodontic SBSS joints was jeopardized, subsequently reducing corrosion resistance. This corroborates with the theories of past investigators such as Bergman et al., (1982), Kim and Johnson (1999) and Shin et al., (2003).

The theory of active-passive cells is thus relevant as the silver solder brazing material beneath such salt deposits (precipitates) was evidently subjected to corrosive attack. This concurs with the Galvanic Series (Appendix A) since passivity of the orthodontic SBSS joints decreased and the electrochemical potential between the stainless steel wires and the silver solder increased, especially when exposed to Fusayama's artificial saliva.

Furthermore, according to Hwang et al., (2001), orthodontic alloys emitting electrogalvanic currents with saliva as the medium, produces a release of metal ions. Von Frauhofer (1997) has stated that the release of such metallic ions elicits adverse patient reactions, many of which have been reported in the literature (Dunlop et al., 1989 and Bishara, 1995). However, the release rate of metallic ions is not proportional to their concentration but depends mainly on the alloy's corrosion resistance during intra-oral exposure (Zinelis et al., 2004). In other words, the elution of Cu and Zn is indicative of the impaired corrosion resistance of orthodontic SBSS joints.

Relative to the EMF series (Appendix A), Cu and Zn have lower electrode potentials than Ag and will therefore have a greater tendency to dissolve into solution. This unquestionably enhances the corrosion behaviour of orthodontic SBSS joints, which correlates with the atomic absorption results of Cu going into solution (Section 4.7, Figure 4.4). Furthermore, K, S and Ca peaks were evident (Plate 5.2) and this implicates Fusayama's artificial saliva as an aggressive medium that promotes corrosion under prolonged exposure conditions.

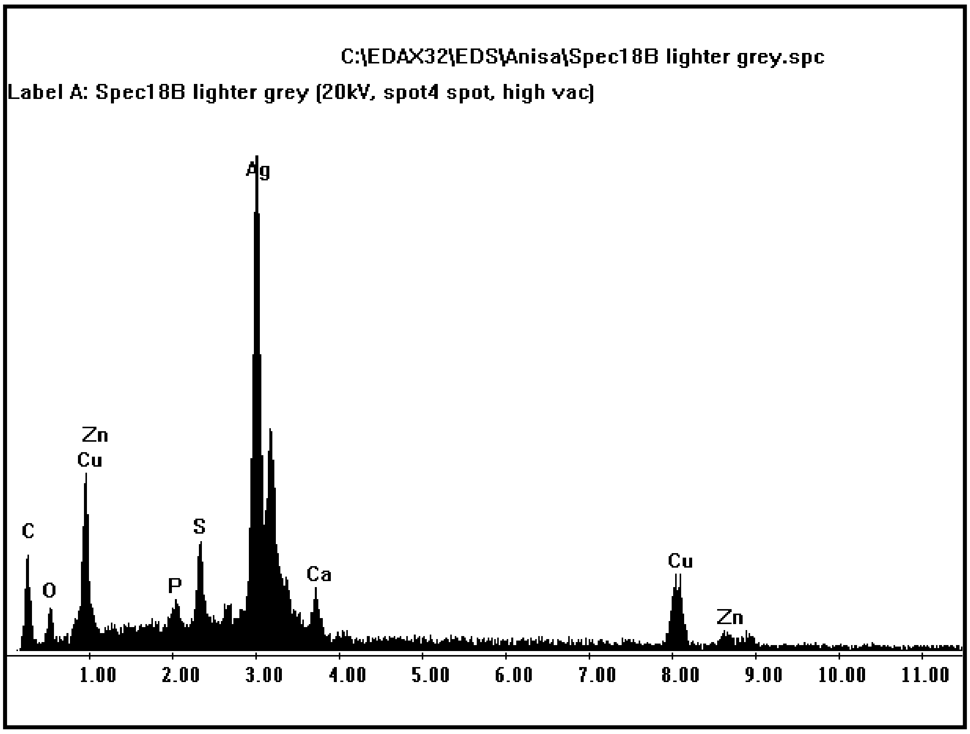


Plate 5.2: EDS of the external surface of orthodontic SBSS joint

The high incidence of Fe precipitates on the external surfaces of the orthodontic SBSS joints confirmed that the stainless steel wires were also prone to corrosion. However, the degree of corrosion, when compared to that observed on the silver solder material was significantly less. This is consistent with previous findings by Berg et al., (1982) and Gjerdet and Hero (1987).

5.3.3.2 INTERFACIAL SURFACE OF THE ORTHODONTIC SBSS JOINT

According to Shigeto et al., (1991), the interface of the brazed joint is greatly weakened as a result of the high density of the galvanic current between the dissimilar metals, regardless of whether it is mechanical connection or alloy union. Such a weakened joint often results in failure from advanced corrosion during clinical use over prolonged exposure. This study concurs with this postulation since morphologically, in cross section, orthodontic SBSS joints (at the interface) reinforced that the combined effects of, (i) electrolyte composition, (ii) degree of electrolyte percolation and electrochemical potential, (iii) metallurgy of the brazing filler material, and (iv) prolonged exposure periods, provide suitable conditions that exacerbated the corrosion tendencies of orthodontic SBSS joints. This further encouraged the elution of Cu, Fe and Ca precipitates, to the extent that crystal growth advanced into the porosity along the interface (Plate 4.12/2).

Moreover, the orthodontic SBSS joint interfaces of the sprayed sample groups were morphologically similar to the control sample group in terms of disclosing the porous nature of the silver solder brazing material (Plate 4.9/1 and 2). It is therefore suggested, that overheating of the silver solder brazing material and flux, produces “process related” solder defects such as entrapment of gas pockets and consequent porosities in the subsequent brazed seam (Heidemann et al., 2002). Alternately such porosities may have also developed from the way in which the stainless steel wires pulled away from the silver solder brazing material during fracture. The investigation of these phenomena is beyond the scope of this study and may therefore be a subject for further research.

This study further suggests that the corrosion resistance of orthodontic SBSS joints is faster impaired by the formation of a crack at the external s/w interface (Plate 4.3). This facilitated increased weakening of the silver solder brazing material particularly in a chloride-containing solution such as Fusayama's artificial saliva.

In agreement with Angelini et al., (1991), corrosion products when present at an interface between the silver solder brazing material and stainless steel parent wires surfaces (Plate 4.9 and 4.12) inevitably produces a substantial decrease in the strength of the junction, impairing the overall mechanical and physical properties of orthodontic SBSS joints.

Contrary to the belief that Fusayama's artificial saliva closely approximates normal salivary condition, this study indicated that it can serve to be a much more aggressive medium. An ideal physiological saline simulating normal salivary conditions and one that is highly recommended for in vitro studies therefore constitutes an important area for future research.

5.4 SUBPROBLEM THREE - ASSOCIATION BETWEEN TENSILE STRENGTH, MICROSTRUCTURE AND EXPOSURE PERIOD

Past studies have investigated either the tensile strengths (Laird and von Fraunhofer, 1972; O' Toole et al., 1985; Angelini et al., 1991; Gawlik et al., 1996), metallurgical (Rogers, 1979) and/or corrosion (Mueller, 1981; Berg et al., 1982; Angelini et al., 1991; Kusy, 2000; Heidemann et al., 2002) influences on the microstructure of brazed joints. However, there appears to be no known evidence in support of the association between increased exposure time, particularly in a physiological saline such as Fusayama's artificial saliva, and the microstructure of orthodontic SBSS joints on the propensity towards corrosion that ultimately affects the tensile strength of the orthodontic SBSS joints and inevitably influences the overall intra-oral performance of orthodontic appliances.

Qualitative analysis of elemental composition and surface morphologies reinforces the notion that increased exposure time, affects not only the microstructure of orthodontic SBSS joints, but significantly influences the propensity towards corrosion. Consequently, the hypothesis for the third subproblem was accepted because an association between the exposure periods and microstructure of orthodontic SBSS steel joints was established and their combined effects were shown to irrefutably influence the tensile strengths of orthodontic SBSS joints.

In spite of the impaired function of corroded orthodontic appliances, there may be several biological implications that may adversely affect patient well-being. This is of concern to clinicians since oral manifestations in the form of lesions (Bishara, 1995) and allergic responses (Dunlop et al., 1989) have been reported. Although orthodontic removable appliances are usually worn for a short term only, the presence of such clinical signs should not be ignored, since clinical manifestation is often indicative of the elicitation of metal ions.

This study concurs with Zinelis et al., (2004) that the selection of an optimum brazing alloy, especially to dental technicians, “is a real challenge as the material selected for brazing should fulfil a wide range of metallurgical, corrosion resistance, and biological criteria”, which ultimately affects the tensile strengths of the orthodontic SBSS joints.

It is therefore proposed that in order for dental manufacturers to remain strategically viable on the competitive dental market, an alternative brazing material be provided or the metallurgical properties of their present silver solder brazing material used in orthodontic SBSS joints be improved. This new and/or improved brazing material should be (i) galvanically compatible with stainless steel, (ii) readily passivated and (iii) free of elements with adverse biological effects (Zinelis et al., 2004).

In light of the above, this study clearly recognised the galvanic incompatibility between silver solder and austenitic stainless steel wires as it induces enhanced surface roughness and change in metallurgical characteristics of orthodontic SBSS joints. In addition, it must be taken into consideration that the orthodontic SBBS joints in this study were unloaded, but under intra-oral conditions will experience other stresses, which will undoubtedly exacerbate corrosion, thereby weakening the strength of the joint.

CHAPTER SIX

Few people are capable of expressing with equanimity opinions which differ from the prejudices of their social environment. Most people are even incapable of forming such opinions.

Albert Einstein (1879 – 1955)

6. CONCLUSIONS/APPLICATION OF FINDINGS

6.1 ULTIMATE TENSILE STRENGTH

The statistical difference in the mean tensile strength values of orthodontic SBSS joints between the sprayed sample groups and control (unsprayed) sample group conclusively indicated that:

- In orthodontic brazing, complete coverage of the stainless steel wires by the silver solder brazing material, accompanied by a high surface lustre, positively improves the mechanical and clinical properties of orthodontic SBSS joints.

- The tensile strength of orthodontic SBSS joints were significantly reduced as a result of galvanic corrosion phenomena.

- The substantially short time period employed for this in vitro investigation along with the increased presence of diluted precipitates significantly precluded the extrapolation of quantitative results on the tensile strengths of orthodontic SBSS joints.

Moreover, in comparison to the control (unsprayed) sample group whereby fracture paths in the weaker silver solder brazing material were observed, orthodontic SBSS joints exposed to Fusayama’s artificial saliva produced observable interfacial fracture paths, which is indicative of the reduced tensile strengths of the orthodontic SBSS joints.

6.2 MICROSTRUCTURE OF ORTHODONTIC SBSS JOINTS

Through SEM/EDS analysis, this study was able to observe the extent of the surface corrosion and identify microstructural changes of the orthodontic SBSS joints. In some ways new perspectives were afforded and in the same faith, already existing concepts were verified such as:

- In terms of surface morphology, dendritic/lamellae and star/clover patterns were observed by all sample groups. However, surface patterns of the control sample group were smooth as opposed to the sprayed sample groups, which were concave due to the nucleation of Ag-rich phase and dissolution of Cu-rich and Zn-rich phases. This degeneration of the silver solder matrix is further characteristic of a corrosive environment such as Fusayama's artificial saliva, which reduces the mechanical properties of orthodontic SBSS joints.

- In cross section, the integrity of the orthodontic SBSS joints demonstrated the porous nature of the silver solder brazing material that favoured increased localised corrosion in Fusayama's artificial saliva. This encouraged corrosion to advance along the interface and promote the progression of crystal growth into the porosities.

6.3 ASSOCIATION BETWEEN TENSILE STRENGTH, MICROSTRUCTURE AND EXPOSURE PERIOD

The findings of this study confirm that an association between exposure periods and microstructure of the orthodontic SBSS joints exists and that their combined effects positively influence the tensile strengths of orthodontic SBSS joints. Moreover, the propensity towards corrosion is potentiated.

The findings of this study have explicitly underlined the need for dental manufacturers of silver solders to improve their present products or alternately develop an improved solder for brazing orthodontic wires. Herein lies an important area for future research.

6.4 APPLICATIONS OF FINDINGS

For the commercial dental technician this study has highlighted the following with regards to brazing with silver solder:

Brazed joints in removable orthodontic appliances such as the Hawley appliance are usually located in the non-aesthetical areas. Therefore, dental technicians are to ensure that after brazing, the stainless steel parent wire surfaces must be completely covered by the silver solder brazing material and that a brazed joint length of more than 4mm is desired. This will improve the mechanical properties of orthodontic SBSS joints and ultimately influence long term clinical success.

The tensile strength results of orthodontic SBSS joints clearly indicated that torch flame soldering, although quick and cost effective, does not produce uniform joints. Dental technicians should therefore strictly adhere to proper technical procedures when brazing orthodontic stainless steel wires using a torch flame, as this significantly reduces the propensity towards corrosion.

After brazing, orthodontic SBSS joints must be smooth and highly polished, whilst ensuring that the stainless steel parent wires remain enclosed by the silver solder brazing material. This significantly contributes to long term clinical success of the appliance in the mouth. Moreover, it minimizes the manifestation of oral lesions.

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APPENDICES

APPENDIX A

APPENDIX B - 1995 ANNUAL BOOK OF ASTM STANDARD, Vol. 03.02,

B117 – 94: STANDARD PRACTICE FOR OPERATING SALT SPRAY (FOG) TESTING APPARATUS

Practice B 117 is most useful in estimating the relative behavior of closely related materials in marine atmospheres, since it simulates the basic conditions with some acceleration due to either wetness or temperature or both.

EXPOSURE CHAMBER

1. The reservoir must be made from a corrosion–resistant material and be constructed so no “condensation” products of the salt fog can drip into the reservoir.

2. The compressed air entering the atomizers shall be filtered to remove all impurities. Means shall be provided to humidify and heat the compress air, as required. The air pressure shall be constant with ± 700 Pa and sufficient to produce a finely divided salt solution fog.

3. The reservoir to be suitably heated by means of an immersion heater and its temperature controlled by means of a thermostat.

4. Specimens shall not contact each other or other metallic material or any material capable of acting as a wick.

5. Each specimen shall be placed so as to permit free setting of fog on all specimens.

6. Salt solution from one specimen shall not drop on any other specimen.

pH and Temperature

1. When the pH of the solution is adjusted to room temperature and atomized at 37°C, the pH of the collected solution will be higher than the original due to the loss of CO_2 at the higher temperature. It is therefore necessary to adjust it below 6.5 so the collected solution after atomizing at 35° - 37°C will meet the pH limits.

2. However heating the H_2O from which the salt solution is prepared to 35°C or above, to expel CO_2 and adjusting the pH of the salt solution within the limits of 6.5 to 7.2 produces a solution, the pH of which does not materially change when atomized at 35°C (95°F).

3. The pH can be adjusted by additions of dilute cp hydrochloric acid or cp sodium hydroxide solutions.

4. The compressed air supply to the nozzles for atomizing the salt solution to be free of oil and dirt by means of a commercial cartridge filter, which includes an expiration indicator, and maintained between 69 and $172kN/m^2$ (10 to 25 psi).

CONDITIONS OF THE SALT – SPRAY CHAMBER

1. Temperature – the temperature of the exposure zone of the closed cabinet shall be recorded twice daily at least 7hours apart (except on Sundays, Saturdays and holidays when the spray test is not interrupted for exposing, rearranging or removing test specimens or to check and replenish the solution in the reservoir).

2. The temperature must be recorded with the salt–spray chamber closed to avoid a false low reading because of the wet–bulb effect when the chamber is open.

3. Nozzle to be directed so that none of the spray can impinge directly on the test specimens.

CLEANING OF TEST SPECIMENS

Also recommended is cleaning of the specimens by gentle washing or dipping in clean running water not warmer than 38°C to remove salt deposits from the surface and immediately dried.

APPENDIX C - DISCUSSION OF IMPORTANT FACTORS THAT AFFECTED THE MATERIALS AND METHODS

The following section provides reasons on the use of certain techniques, materials or items of equipment. The fundamental importance of this section is that it offers an explanation of methods used in the preliminary investigations that may have had a critical bearing on or may have affected the method that was outlined in section (3.4).

1. PRELIMINARY STUDY-PART ONE (COMPLETED ON 5 JUNE 2001)

1.1 METHOD SELECTION

In the literature related to this study, there was limited information to the type of instrumentation used for in vitro studies in determining the period taken before the strength of the orthodontic SBSS joints is compromised.

To ascertain the sample sizes and immersion periods, a database of related studies was used to produce significant representation of the total sample size of orthodontic SBSS joints and immersion periods. The study further attempted to conform within parametric statistical evaluation and therefore increased the sample size in order to improve the reliability of other studies but to stay within the feasibility of this study. Therefore it was decided that:

I. Four periods of immersion times notably; 30, 60, 90 and 120 days were used.

II. Two hundred orthodontic SBSS joint specimens were produced. Fifty specimens assigned to each time period.

III. At that time in the study (2000), lack of reliable data on simulated electrolyte systems warranted the study to review electrolytes used in previous studies and is as follows:

PREVIOUS STUDIES (YEAR)	SOLUTION
Angelini et al. **(1991)**	Artificial Saliva & Ringer's solution
Berge et al. **(1982)**	0.9% NaCl & Ringer's solution
Brockhurst and Pham **(1989)**	0.9% NaCl in water
Mueller **(1981)**	1% Hydrogen Peroxide & Artificial Saliva

Taking the above into consideration and after much consultation with various leading local medical professionals (Dr. Strini Naidoo, 2000), it was further reaffirmed that Ringer's solution was an acceptable physiological saline commonly employed in most in vitro experiments. Ringer's solution (Table 1), an aqueous solution of the chlorides of sodium, potassium and calcium (similar to saliva) was selected as the immersion medium for the study. This solution was kept at pH 8 and was changed weekly. The in vitro machine required 33 litres of solution per week in order to ensure that the orthodontic SBSS joint specimens were completely immersed (Plate 1).

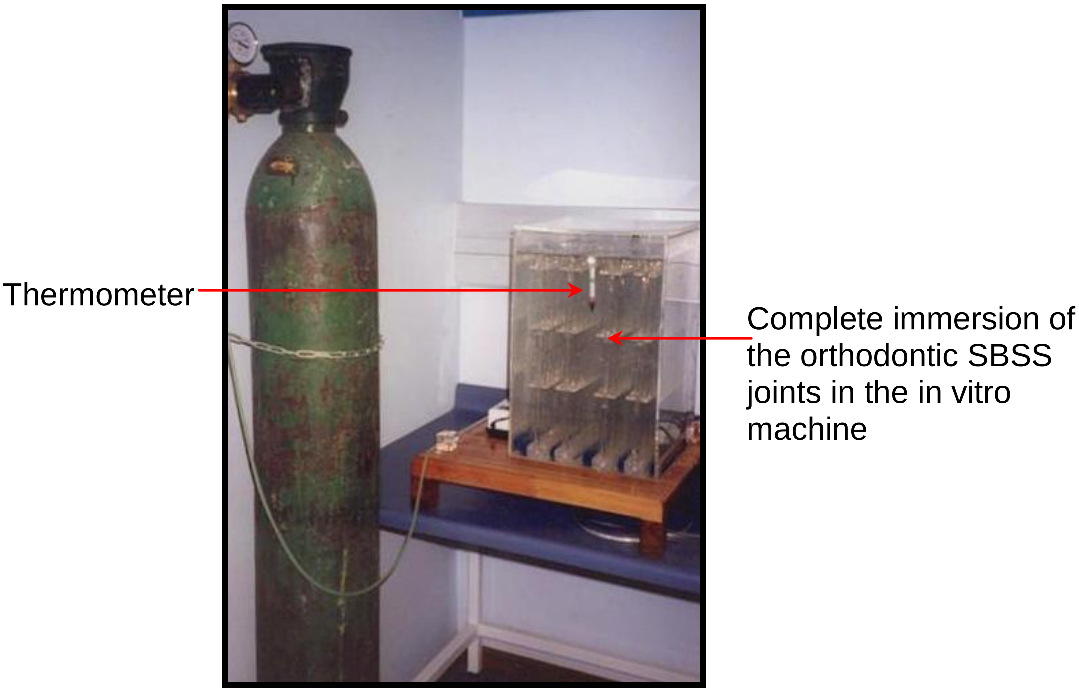


Plate 1: In Vitro machine

IV. The in vitro machine heated the Ringer's solution to 37°C and had received a regulated flow of carboxygen (oxygen and carbon dioxide).

Table 1: Composition of Ringer's solution

CHEMICAL	FORMULA	QUANTITY
Sodium Chloride	NaCl	6.5 g/l
Potassium Chloride	KCl	0.15g/l
Calcium Chloride	CaCl	0.12g/l
Sodium Bicarbonate		0.2g/l
Glucose		0.5g/l
1 Litre of Distilled Water		

1.2 ORTHODONTIC JIGS

To take account of the variance associated with the brazing and testing procedures and to produce specimens that were of the exact same dimensions, three specifically engineered jigs were manufactured by the Department of Mechanical Engineering (Steve Biko Campus, Durban Institute of Technology, Durban, South Africa). The three jigs (Section 3.5, Plate 3.2) are defined as follows:

- A Bending Jig – ensured that each orthodontic stainless steel wire was shaped of equal length, breath and height. An average bridge length of an Adams clasp® is 8 mm (Claassen, 2000). Hence, the bending jig also accommodated for the desired orthodontic SBSS joint length of 8 mm. The design of the jig also attempted to minimise any surface damage caused by the bending process which would affect the tensile results later by creating artificial stress raisers.

- A Brazing Jig – allowed for the accurate placement, assembly and contact of the orthodontic stainless steel wires during soldering thereby ensuring the correct gap distances between the stainless steel wires.

- Clamping Jigs – were used to engage and firmly hold the test specimens during tensile testing of the orthodontic SBSS joints. This facilitates correct and meaningful tensile strength measurements. The design was such that the 0.7mm wires were not loaded at their clamped position, but the load was distributed by frictional means over a long length of wire. This helps minimise the effects of wire elongation reducing the cross sectional area of the wire and causing failure, but more importantly ensured that no high stress points were transmitted to the specimens. The result of the care taken in the design of the jigs is that every single specimen would fracture at the brazed joint and not near or in the grips.

In addition, stainless steel are considered poor conductors of heat, therefore the jigs were produced from this material. This is crucial, especially in the brazing process, since they draw the least heat away from the joint (Aufhauser Brazing Procedures Online, 2003).

1.3 FAILURE OF ORTHODONTIC SBSS JOINTS

The 200 orthodontic SBSS joint specimens had experienced severe corrosion activity that resulted in the preliminary study failing after one month of testing. Tensile testing of specimens on the Instron Universal Testing machine was not possible as the specimens separated in the in vitro machine. No measurable statistics were obtained.

The scanning electron microscopy and energy-dispersive spectroscopy (SEM/EDS) and the surface morphology microphotograph (Plate 2) of the failed orthodontic SBSS joint, obtained through the scanning electron microscope, were in support of each other. They highlighted that the high salt content of the Ringer's solution largely contributed to the extensive corrosion experienced by the orthodontic SBSS joints that is evident by the presence and increased accumulation of corrosion precipitates.

This was confirmed by Hack (member and past chairman of the ASTM *(American Standard for Testing Materials)* Committee - G01 on Corrosion of Metals, 2002) who reported that the electrical conductivity of Ringer's solution was sufficient to enhance galvanic corrosion caused by material differences between the stainless steel and the brazing material. Therefore, Ringer's solution was replaced by Fusayama’s artificial saliva of pH 8 as the medium for the preliminary study – part two.

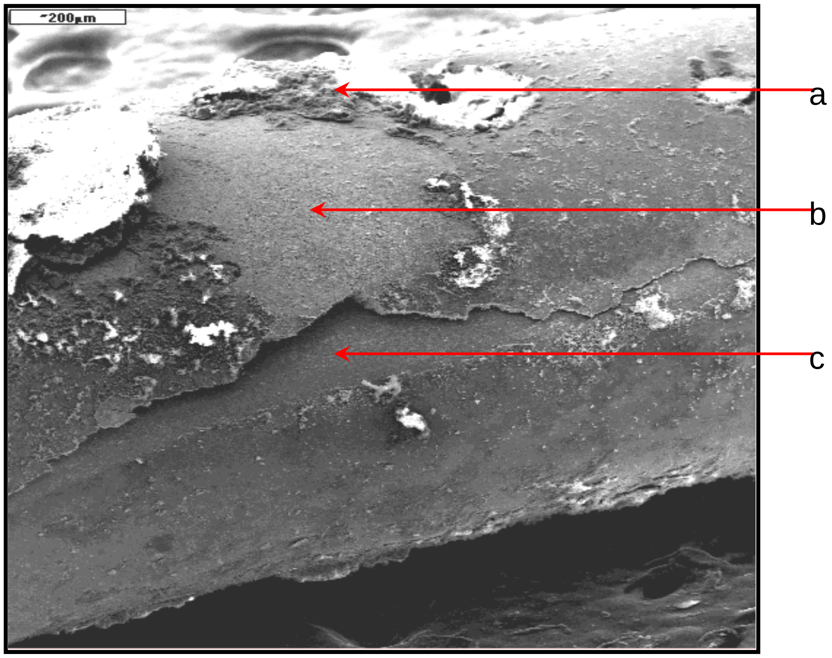


Plate 2: Failed orthodontic SBSS joint with an increased accumulation of corrosion precipitates

a – Precipitate,

b – Silver solder, and

c – Stainless Steel wire

Scale bar: 200 µm

2. PRELIMINARY STUDY-PART TWO
(COMPLETED ON 27 MAY 2002)

Due to the time and budget constraints, twenty orthodontic SBSS joint specimens were fabricated, of which 5 specimens were removed at four time periods: 7, 14, 21 and 28 days. After the 28 day period a further 5 specimens of the control (unsprayed) group were produced.

2.1 FACTORS CONSIDERED IN QUANTIFYING FUSAYAMA'S ARTIFICIAL SALIVA TO NATURAL SALIVA

Every attempt was made to quantify artificial saliva in order to simulate conditions normally present in the mouth. Fusayama's artificial saliva of pH 8 was used as the medium, which was filtered to remove all impurities prior to delivery of the medium into the atomizers (ASTM Standard, 1995: B117).

The medium was maintained at 37°C in order to simulate the accepted physiological temperature believed to be in the mouth. A thermometer and pH meter was used to daily monitor the temperature and pH of the artificial saliva respectively. The temperature and pH monitoring was recorded daily (Appendix G). A regulated flow of carboxygen (95% oxygen and 5% carbon dioxide) was bubbled into the artificial saliva, since the flow of carboxygen helps to create turbulence that disperses heat from the heating element. Ultraviolet light was used as a precautionary measure against bacterial contamination.

The composition of the Ringer’s solution used for preliminary study – part one greatly influenced the magnitude and conductivity of the galvanic current. This increased the susceptibility to corrosion, resulting in failure of the orthodontic SBSS joints. Von Fraunhofer (1994: v2: 160 & 161) also noted metals having a potential difference greater than 50mV between them was harmful and is associated with pathological effects arising from galvanic cells. This promotes the occurrence of oral lesions in the mouth.

Due to the possible potential implications on the susceptibility to corrosion, a voltmeter was used daily to monitor the magnitude of the galvanic current existing between the brazed specimens in the in vitro machine. However, it is noted that this is not a means of quantifying or even predicting the severity of bimetallic corrosion as galvanic rates require to be reliably obtained by direct measurement using zero–resistance ammeters or potentiostats (Pryor & Astley, 1994: v1: 221)

In order to simulate actual conditions in the mouth, the saliva was sprayed on the orthodontic SBSS joint specimens. The sprayed samples were removed from the bath daily for 1 hour; since it was assumed that exposure to air would stop any crevice corrosion initiated during the wet part of the cycle. At the present time, there is no data available that indicates the optimal time-period required for the specimens to be kept outside the machine in order to prevent crevice corrosion (Hack, 2002).

2.2 TESTING MACHINE CONSIDERATIONS

Tensile testing of the samples was done in the Department of Dental Services (Steve Biko Campus, Durban Institute of Technology, Durban, South Africa) on an Instron Universal Testing Machine (Model 1122, Instron Corp., High

Wycombe, Bucks, UK – Plate 3). According to Gillis and Gross (as cited in Waddell, 1993), the rate at which a specimen is deformed (strain rate) is an important consideration in the testing of a material as the strength properties tend to increase at higher rates of deformation.

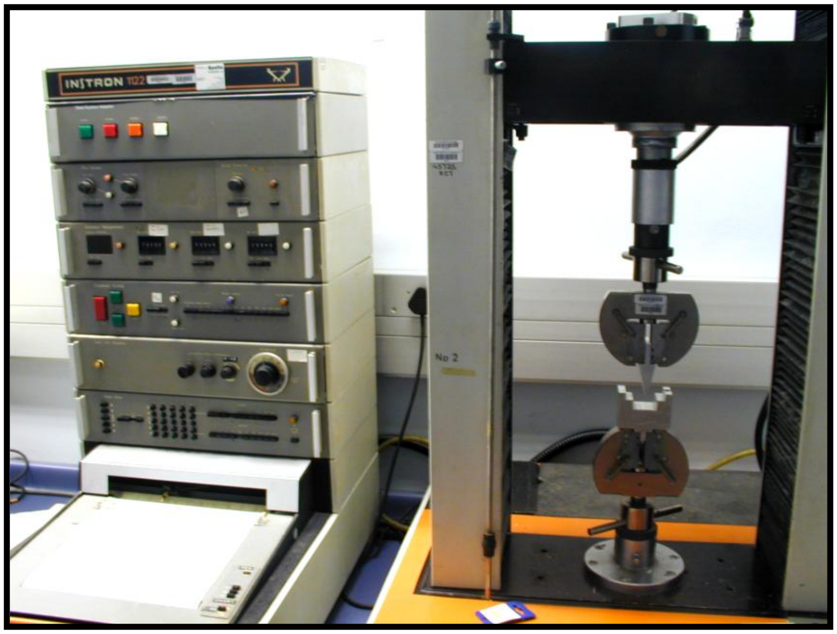


Plate 3: Instron Tensile Testing Machine

ISO 9333: 1990 (E) (Appendix J) specify that the specimens should be loaded at a cross head speed of (1.5 ± 0.5) mm/min up to the fracture point of the specimen. However, on reviewing related literature in the past two decades (hence the use of older references), specifically in terms of brazing, it was found that the crosshead speeds used in previous studies ranged as follows:

PAST STUDIES (YEAR)		CROSS HEAD SPEED
Gawlik et al.	(1996	2.0mm/min
Angelini et al.	(1991)	0.5mm/min
Waddell	(1993)	1mm/min
O'Toole et al.	(1985)	2.5mm/min

Kaylakie and Brukl(1985)	1mm/min

Taking the above into consideration, it was decided that for this study a crosshead speed of 2mm/min was suitable as most studies ranged from 0.5mm/min to 2.5mm/min. After fracture, the orthodontic SBSS joints were visually examined to determine whether the fracture had occurred at the solder/wire (s/w) interface or in the solder material. It was noted that the fractured orthodontic SBSS joint specimens exhibited a combination of the above fractures.

2.3 OUTCOMES OF PRELIMINARY STUDY – PART TWO

The following results are not an in-depth study of the tensile strengths and metal (ions) element content of the orthodontic SBSS joints. The sole purpose of this investigation was to find an improved method, which would address the problem statement of the final investigation.

I. No premature fractures of the orthodontic SBSS joints were observed during the entire period of the investigation. Although the orthodontic SBSS joints were severely tarnished, very little corrosion of the samples had occurred.

II. The Universal Instron Tensile testing machine produced measurable tensile strength values of the orthodontic SBSS joints, recorded in Newton's. This is summarised in Table 2.

III. Drop in pH from 8 to between 7.4 – 7.8 were noted (Appendix G). This decrease was attributed to liquid evaporation caused by the spray system. A daily measurement of pH and also maintenance of temperature at 37°C were adopted for the new design.

IV. This finding was confirmed by SEM/EDS of the orthodontic SBSS joints; because of the use of ultraviolet light, the joints did not suffer any bacterial invasion. Low levels of Cl and acceptable levels of Ag (main constituent of solder) and Fe (main constituent of stainless steel) were observed in the SEM analyses.

V. The loss of silver solder mass only increased after longer periods of exposure in the in vitro machine. This was confirmed by Claassen (NHDip. Dental Tech. (Status TN); NHDPSE (CT); Reg. Dental Tech. and part – time orthodontics laboratory owner for the past ten years, 2002) who noted that the removable orthodontic appliances received for repairs of the SBSS joints experienced mass loss of the solder material after placement in the mouth.

Table 2 – Summary of the ultimate Tensile Strength (N) for preliminary study- part two

SPECIMENS	**CONTROL**	**TIME PERIODS**			
		7 DAYS	**14 DAYS**	**21 DAYS**	**28 DAYS**
1	301.7	136.6	296.20	292.10	307.1
2	236.3	284.0	461.20	*54.15	268.5
3	386.9	289.9	333.30	336.30	*358.5
4	248.7	356.9	237.20	196.00	274.4
5	259.6	159.4	*49.86	188.50	293.2
***Specimen rejected**					

In conclusion, the outcomes of this preliminary study allowed the following to be incorporated into the new experimental design for the final investigation:

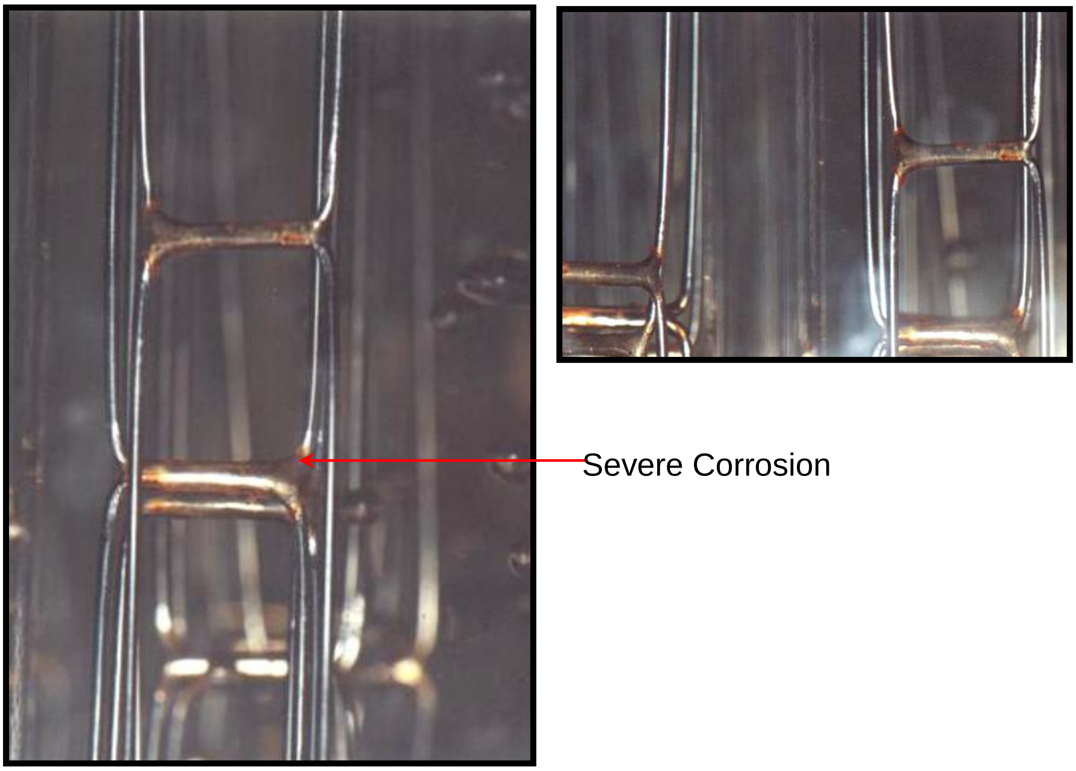
I. As opposed to complete immersion, the sample spraying technique proved successful. The technique was therefore considered suitable for the new study.
II. Fusayama's artificial saliva was established as the medium of choice. To overcome any loss of liquid during the experimental phase, Fusayama's artificial saliva was changed weekly.
III. Although no bacterial contamination of the specimens was observed, as a precautionary measure, the use of ultra violet light was introduced.

APPENDIX D - RESULTS OF PRELIMINARY STUDIES

PRELIMINARY STUDY - PART ONE

1. VISUAL OBSERVATIONS OF THE ORTHODONTIC SBSS JOINTS

In the first week of immersion, visible corrosion in the form of brown corrosion products was evident on all of the orthodontic silver SBSS joints (Plate1). With increase exposure time it appeared that the corrosion tendency became progressively severe by evidence of the disintegrating thickness of solder material around the wires, as confirmed by SEM analysis (Plate 2) and by the presence of green deposits.



Severe Corrosion

Plate 1: Severely corroded orthodontic SBSS joints under complete immersion in the in vitro machine

Severe corrosion activity resulted in the silver solder disintegrating and the parent metal wire exposed

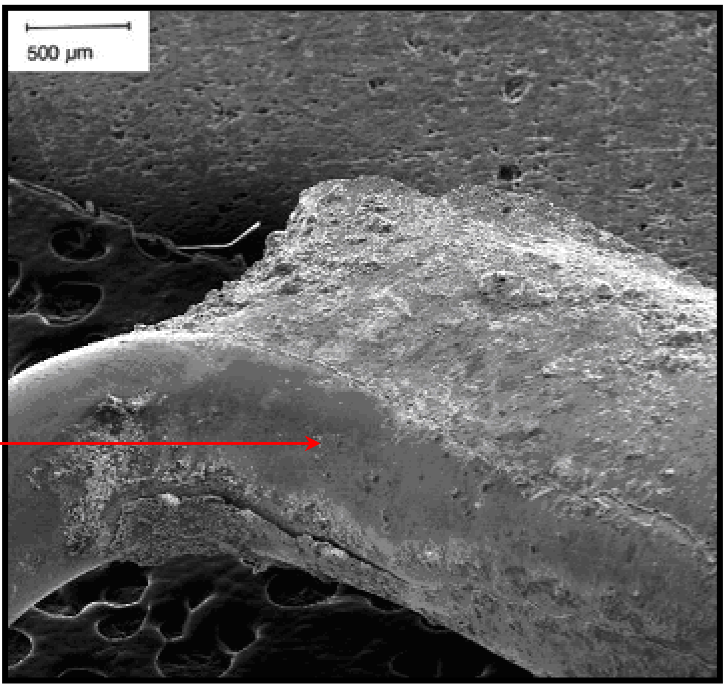


Plate 2: Disintegration of Silver Solder from the parent wire surface
Scale bar: 500 µm

By the third week of immersion, appreciable amounts of Cu precipitates were grossly evident and about ± 50% of the total number of 200 brazed specimens had separated in the immersion tank. This severely compromised the tensile strength of the orthodontic SBSS joints and hence no measurable values for tensile strength were possible.

2. MICROSTRUCTURAL ANALYSIS OF THE ORTHODONTIC SBSS JOINTS

The surface morphology and deterioration of the orthodontic SBSS joint specimens was observed by SEM/EDS analysis. The corroded specimens demonstrated the following:

- All brazed specimens were significantly tarnished (n = 200) and the presence of dissimilar metals (silver solder and stainless steel) promoted galvanic corrosion (Park and Shearer, 1983).

- Regardless of the presence of brown deposits, the surface of the stainless steel wires was generally in a good condition. Analysis of these brown deposits showed them to consist predominantly of Fe and O, indicating that some corrosion of the steel was occurring.

- It was evident that the solder was being preferentially attacked due to the observable disintegration of the solder material from the wire surfaces.

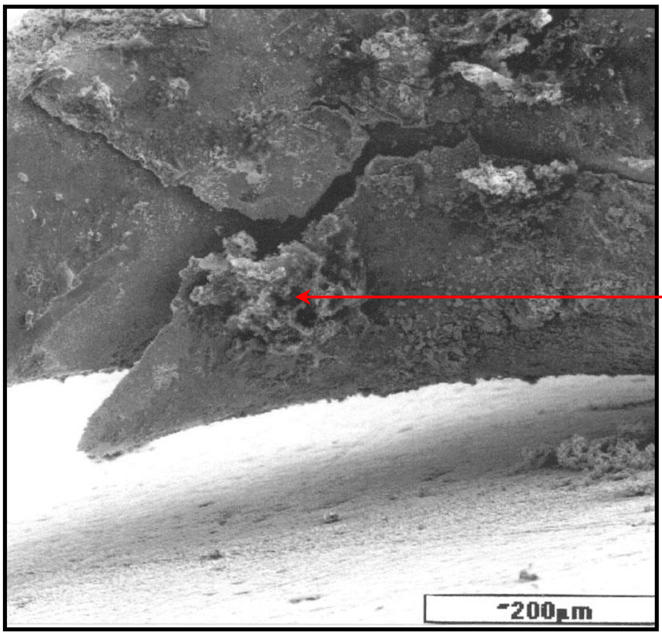
- Green deposits apparent on the surface of the solder consisted mainly of Zn, Cu and O.

- At the solder/wire (s/w) interface, there were large copper-coloured regions, which was predominantly of copper.

- Cu, Fe, Zn and Cl precipitates were largely present on the surfaces of the brazed joints (Plate 3). Cl was found to be in excess of the acceptable level of 0.05% (Park and Shearer, 1983).

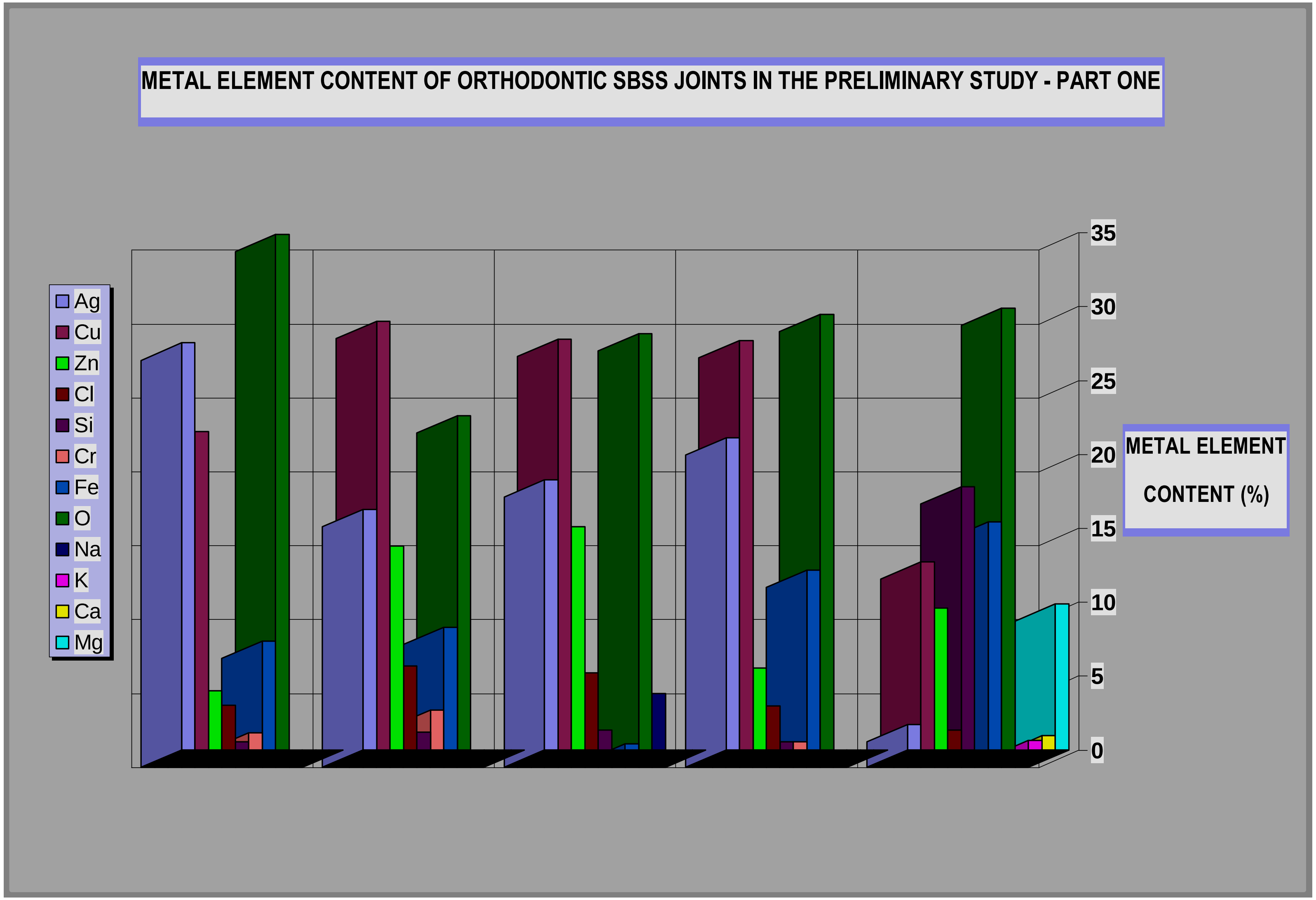
- SEM/EDS analysis further revealed Na, Ca, Mg and K peaks and these elements were discernable with increased exposure time. The possible implication was that the Ringer’s solution and method of complete immersion combined with increased exposure time positively enhanced corrosion susceptibility. Graphs 1 and 2 specifically reflect the substantial differences in the metal element content, present on the external surfaces of the orthodontic SBSS joints, between immersed sample groups and the control (unimmersed) sample group respectively.

All of the above positively promoted the failure of orthodontic SBSS joints.

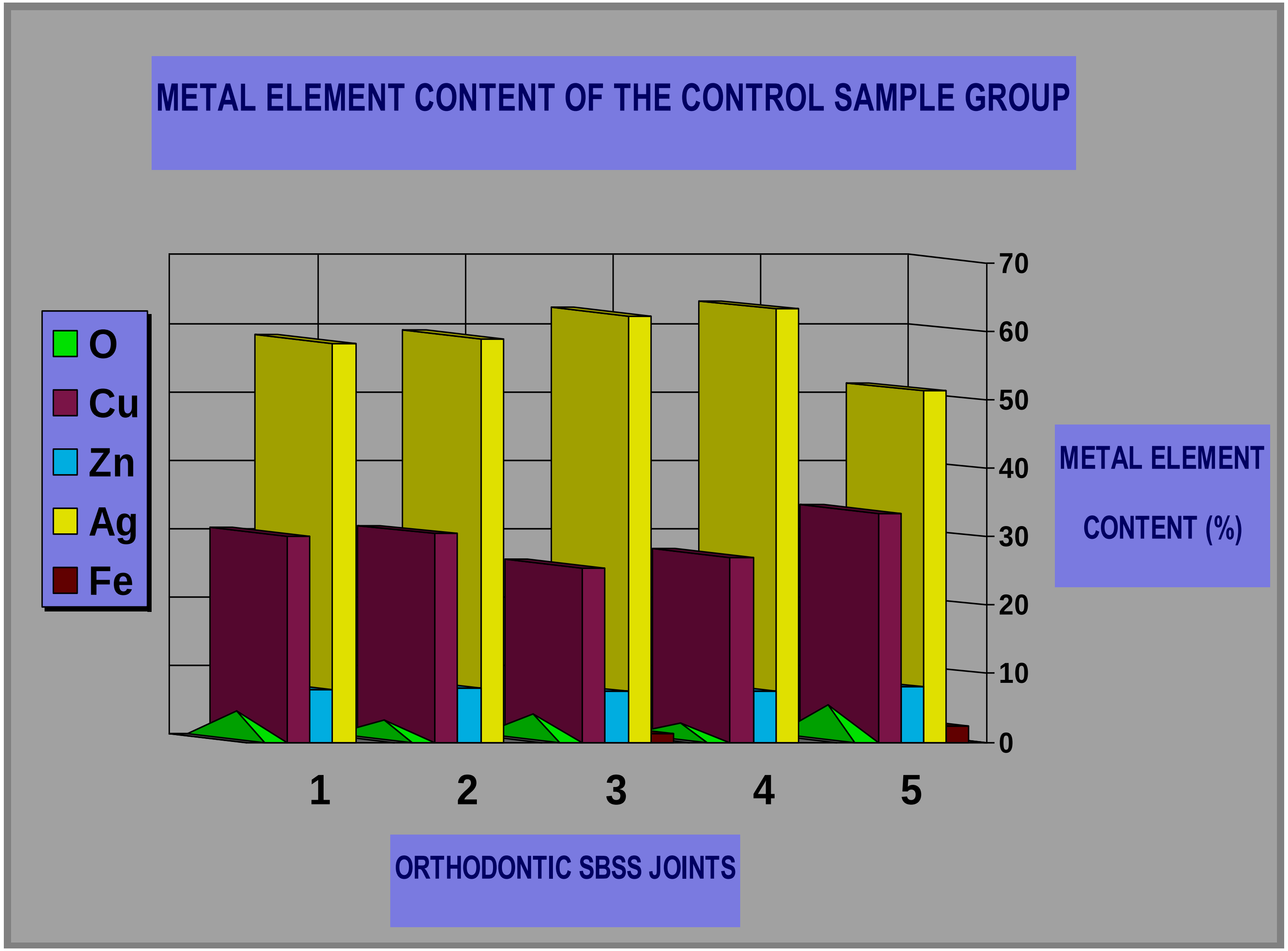


Combination of Cu, Cl, Fe and Zn precipitates present on the external surfaces of the orthodontic SBSS joints.

Plate 1: Presence of precipitates on the orthodontic SBSS surfaces
Scale bar: 200 µm



GRAPH 1: Metal element content of orthodontic SBSS joints in the Preliminary Study – Part One

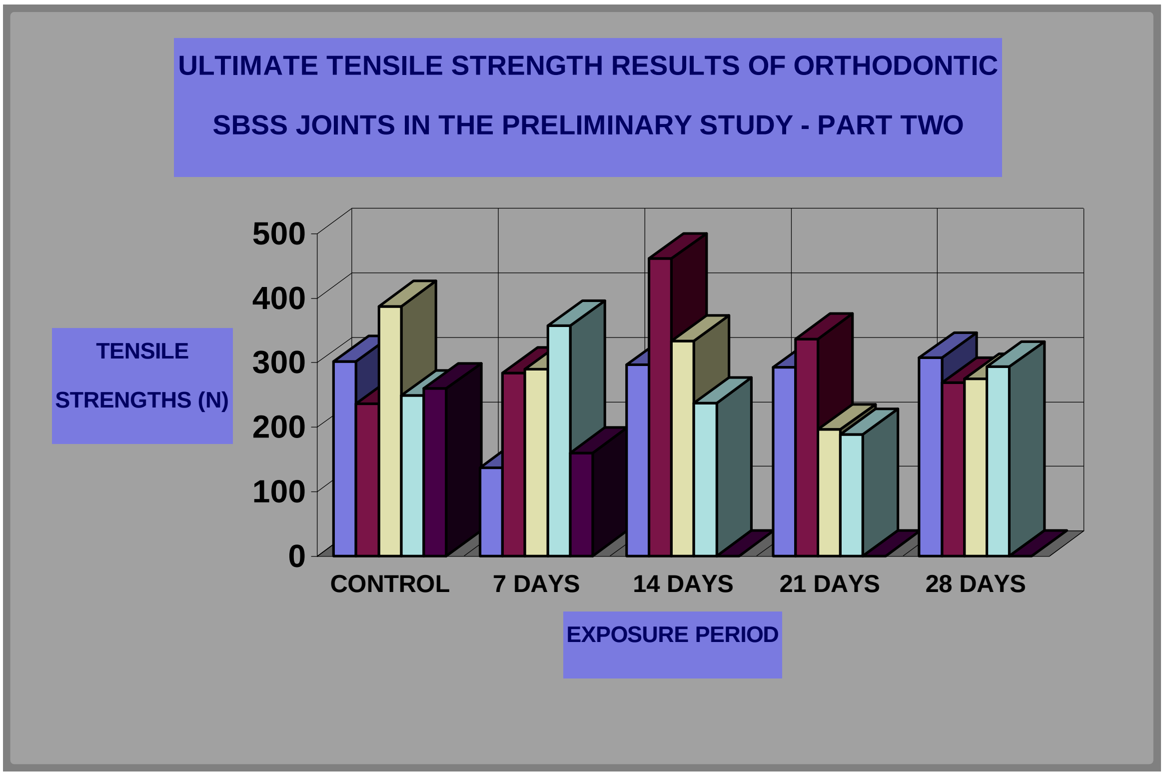


GRAPH 2: **Metal element content of the Control sample group**

PRELIMINARY STUDY - PART TWO

The primary reason for this preliminary study was to test and assess the new and improved methodological design. Therefore no statistical calculations were applied. Corrosion of the orthodontic SBSS joints was visible but was not as aggressive as in the preliminary study - part one. As a result measurable tensile strength values were obtained (Appendix C – Table 2).

Graph 3 clearly demonstrates the ultimate tensile strength values of the orthodontic SBSS joints. The data obtained from this study positively demonstrated that the improved methodological design of the in vitro machine and the use of Fusayama's artificial be accepted for the final investigation.



Graph 3: Ultimate tensile strength results of the orthodontic SBSS joints in preliminary study - Part Two

WEEK ONE- 7 APRIL TO 13 APRIL 2003

DATE&DAY	TIME	pH(with)	pH(without)	TEMP.	VOLTAGE	COMMENTS
MONDAY						In vitro investigation commenced at 13:30
07/4/2003	17:00	8.2		37°C		
TUESDAY						
08/4/2003	7:20	6.5		35°C	6 – 10mV	Specimens removed from machine at 12:30
	13:40		7	32°C		Specimens returned to machine at 13:45
WEDNESDAY						
09/4/03	7:50	7.7		34°C	3mV	Specimens removed from machine at 12:45
	12:25		8.4	32°C		Specimens returned to machine at 14:30
THURSDAY						
10/04/03	8:00	8.2		32°C	3mV	Specimens removed from machine at 13:00
	14:00		8.3	32°C		Specimens returned to machine at 14:10
FRIDAY						
11/04/03	7:45	8.2		34°C	3mV	Specimens removed from machine at 12:20
	14:05		8.2	32°C		Specimens returned to machine at 14:15
SATURDAY						
12/04/03	12:20	8		34°C	4mV	Specimens removed from machine at 12:30
	14:25		8	32°C		Specimens returned to machine at 14:30
SUNDAY						
13/04/03	9:15	8.5		35°C	6mV	

Note: pH (with) and (without) indicates with specimens in the tank and without specimens in the tank, respectively.

WEEK TWO - 14 APRIL TO 20 APRIL 2003

MONDAY						Artificial saliva replenished and 1st sample group removed and tested 16/04/04
14/4/2003	7:20	8.5		35°C	6- 8mV	Specimens removed from machine at 12:30
	17:50		7.5	35°C		Specimens returned to machine at 13:45
TUESDAY						
15/4/2003	7:25	8.2		35°C	6 – 8mV	Specimens removed from machine at 11:45
	13:45		7.9	35°C		Specimens returned to machine at 13:50
WEDNESDAY						
16/4/03	7:45	8.2		35°C	6 – 8mV	Specimens removed from machine at 12:20
	14:00		8.1	33°C		Specimens returned to machine at 14:10
THURSDAY						
17/04/03	10:50	8.3		34°C	6 – 8mV	Specimens removed from machine at 12:30
	13:45		8.2	34°C		Specimens returned to machine at 13:45
FRIDAY						
18/04/03	10:00	8.2		32°C	6mV	Specimens removed from machine at 10:05
	11:00		8.2	32°C		Specimens returned to machine at 11:10
SATURDAY						
19/04/03	14:30	7.8		32°C	8 – 10mV	Specimens removed from machine at 14:40
	15:25		7.98	32°C		Specimens returned to machine at 15:35
SUNDAY						
20/04/03	9:00	8.5		35°C	8mV	

WEEK THREE – 21 APRIL TO 27 APRIL 2003

WEEK FOUR - 28 APRIL TO 4 MAY 2003

MONDAY						Artificial saliva replenished. Machine switched off and cleaned between 10:30 – 11:35.
28/4/2003	12:30	7		28°C	6- 8mV	Specimens removed from machine at 11:35
	17:00		7	32°C		Specimens returned to machine at 12:45
TUESDAY						3rd sample group removed and tested 22/04/04
29/4/2003	7:40	8		34°C	4 – 6mV	Specimens removed from machine at 13:00
	14:30		7.7	32°C		Specimens returned to machine at 14:45
WEDNESDAY						
30/4/03	7:30	8		34°C	4 – 6mV	Specimens removed from machine at 12:20
	13:10		8	32°C		Specimens returned to machine at 13:15
THURSDAY						Due to evaporation, more artificial saliva was added on 01/05/03
1/05/03	9:50	8.3		33°C	4mV	Specimens removed from machine at 12:00
	13:00		8.2	32°C		Specimens returned to machine at 13:05
FRIDAY						Low voltage due to one stand remaining in machine
2/05/03	8:15	8.3		33°C	2mV	Specimens removed from machine at 12:45
	14:30		8	32°C		Specimens returned to machine at 14:35
SATURDAY						
3/05/03	8:15	8.3		32°C	2mV	Specimens removed from machine at 8:20
	9:30		8.2	32°C		Specimens returned to machine at 9:40
SUNDAY						

4/05/03	7:40	8.3		32°C	2mV	

WEEK FIVE – 5 MAY TO 7 MAY 2003

MONDAY						
5/5/2003	7:15	8		35°C	2mV	Specimens removed from machine at 15:00
	16:40		7.9	32°C		Specimens returned to machine at 16:45
TUESDAY						
6/5/2003	8:45	7.9		33°C	2mV	Specimens removed from machine at 11:30
	12:25		7.8	32°C		Specimens returned to machine at 12:30
						End of experiment. Last sample group removed and tested.

APPENDIX F - SUBPROBLEM TWO QUANTITATIVE RESULTS

Table 1: METAL ELEMENTAL ANALYSIS ON THE EXTERNAL SURFACES OF ORTHODONTIC SBSS JOINTS

WEEK	Zn	Ag	Cu	100%
7 Days	5	64	17	**85**
	5	52	20	**76**
	5	58	16	**79**
	6	39	28	**73**
	12	42	37	**91**
14 Days	0	49	30	**79**
	6	76	12	**94**
	8	68	21	**97**
	6	58	35	**100**
	5	67	16	**88**
21 Days	4	72	9	**85**
	4	69	15	**88**
	6	78	12	**96**
	5	75	14	**93**
	5	65	15	**85**
28 Days	3	42	27	**73**
	4	66	16	**86**
	3	22	15	**41**
	5	63	20	**89**
	5	46	24	**75**
CONTROL	8	58	30	**96**
	8	58	30	**96**
	8	59	30	**97**
	7	62	25	**95**
	8	63	27	**98**

Table 2: METAL ELEMENTAL ANALYSIS ON THE INTERFACIAL SURFACES OF ORTHODONTIC SBSS JOINTS

WEEK	Zn	Ag	Cu	100%
7 Days	8	43	36	**86**
	6	42	28	**77**
	5	56	18	**80**
	7	47	34	**88**
	8	52	33	**93**
14 Days	7	47	28	**82**
	5	44	19	**68**
	7	65	28	**100**
	7	59	24	**90**
	6	73	18	**98**
21 Days	10	51	36	**97**
	4	27	18	**49**
	5	42	26	**73**
	4	28	11	**43**
	4	31	23	**58**
28 Days	11	35	44	**90**
	5	55	23	**83**
	8	53	39	**100**
	8	22	49	**79**
	7	39	24	**69**
CONTROL	8	53	36	**97**
	7	57	35	**98**
	8	50	29	**86**
	9	57	32	**97**
	9	64	28	**100**

Table 3: METAL ELEMENT ANALYSIS ON THE STAINLESS STEEL SURFACES OF THE BRAZED JOINTS

WEEK	Fe	Cr	Ni	100%
7 Days	61	16	7	**68**
	63	15	5	**68**
	65	18	0	**65**
	58	16	0	**58**
	70	18	7	**78**
14 Days	45	10	0	**45**
	66	16	8	**73**
	70	17	8	**78**
	71	1	8	**79**
	68	18	8	**76**
21 Days	62	13	0	**62**
	59	15	7	**66**
	67	16	7	**74**
	56	11	3	**59**
	72	16	7	**79**
28 Days	56	14	7	**62**
	56	14	7	**63**
	63	16	7	**70**
	62	13	4	**66**
	77	7	0	**77**
CONTROL	70	17	8	**78**
	65	17	7	**73**
	72	16	8	**80**
	70	18	8	**78**
	72	18	9	**81**

APPENDIX G

WEEK ONE- 24 APRIL TO 30 APRIL 2002

DATE&DAY	TIME	pH(with)	pH(without)	TEMP.	VOLTAGE	COMMENTS
WEDNESDAY						
24/04/02						In vitro investigation commenced at 16:30
THURSDAY						
25/04/02	08:00	76.5		32°C		Specimens removed from machine at 08:10
	09:10					Specimens returned to machine at 09:25
FRIDAY						
26/04/02	12:15	7.3		33°C	5mV	Specimens removed from machine at 12:05
	13:05		7.4	32°C		Specimens returned to machine at 13:10
SATURDAY						
27/04/02	11:35	7.4		33°C	3mV	Specimens removed from machine at 11:45
	12:45		7.3	32°C		Specimens returned to machine at 12:50
SUNDAY						
28/04/02	11:45	7.4		34°C	3mV	Specimens removed from machine at 11:55
	13:05		7.4	32°C		Specimens returned to machine at 13:10
MONDAY						
29/04/02	12:05	7.4		34°C	4mV	Specimens removed from machine at 12:05
	13:20		7.5	32°C		Specimens returned to machine at 13:30
TUESDAY						
30/04/02	11:45	7.8		35°C	6mV	Specimens removed from machine at 11:50
	13:15		7.9	32°C		Specimens returned to machine at 13:20

Note: pH (with) - specimens were in the tank/ pH (without) - specimens were not in the tank.

WEEK TWO – 1 MAY TO 7 MAY 2002

WEDNESDAY						
01/05/02	**10:20**	**7.9**		**32°C**	**9mV**	**Specimens removed from machine at 10:25**
	11:25		**7.6**	**32°C**		**Specimens returned to machine at 11:35**
THURSDAY						**1st Sample group removed and tested**
02/05/02	**12:00**	**8**		**32°C**	**10mV**	**Specimens removed from machine at 12:00**
	13:25		**7.7**	**32°C**		**Specimens returned to machine at 13:30**
FRIDAY						
03/05/02	**11:20**	**8**		**33°C**	**10mV**	**Specimens removed from machine at 11:25**
	13:40		**8**	**32°C**		**Specimens returned to machine at 13:45**
SATURDAY						
04/05/02	**11:15**	**8**		**32°C**	**11mV**	**Specimens not removed from machine**
SUNDAY						
05/05/02	**10:45**	**7.4**		**34°C**	**12mV**	**Specimens not removed from machine**
MONDAY						**More Artificial saliva added**
06/05/02	**14:15**	**7.9**		**34°C**	**12mV**	**Specimens removed from machine at 14:15**
	13:20		**7.5**	**32°C**		**Specimens returned to machine at 13:25**
TUESDAY						
07/05/02	**10:45**	**7.8**		**35°C**	**16mV**	**Specimens removed from machine at 10:50**
	11:45		**7.8**	**35°C**		**Specimens removed from machine at 11:50**

WEEK THREE – 8 MAY TO 14 MAY 2002

WEDNESDAY						**Filter was changed**
08/05/02	**11:00**	**7.9**		**32°C**	**16mV**	**Specimens removed from machine at 11:05**
	13:15		**7.9**	**32°C**		**Specimens returned to machine at 13:20**
THURSDAY						**2nd Sample group removed and tested**
09/05/02	**13:15**	**8**		**32°C**	**12mV**	**Specimens removed from machine at 13:20**
	14:15		**7.7**	**32°C**		**Specimens returned to machine at 14:25**
FRIDAY						
10/05/02	**10:55**	**7.7**		**33°C**	**20mV**	**Specimens removed from machine at 11:00**
	12:00		**7.6**	**32°C**		**Specimens returned to machine at 12:10**
SATURDAY						
11/05/02	**10:15**	**7.8**		**32°C**	**20mV**	**Specimens not removed from machine**
SUNDAY						
12/05/02	**10:00**	**7.7**		**34°C**	**20mV**	**Specimens removed from machine at 11:00**
	11:15		**7.6**	**32°C**		**Specimens returned to machine at 11:20**
MONDAY						
13/05/02	**11:00**	**7.6**		**34°C**	**12mV**	**Specimens removed from machine at 11:10**
	13:20		**7.1**	**32°C**		**Specimens returned to machine at 13:25**
TUESDAY						
14/05/02	**10:45**	**7.8**		**35°C**	**16mV**	**Specimens removed from machine at 10:50**
	11:50			**34°C**		**Specimens removed from machine at 11:55**

WEEK FOUR – 15 MAY TO 21 MAY 2002

WEDNESDAY						
15/05/02	10:15	7.9		32°C	25mV	Specimens removed from machine at 10:25
	12:00		7.7	32°C		Specimens returned to machine at 12:10
THURSDAY						3rd Sample group removed and tested
16/05/02	9:55	7.6		32°C	26mV	Specimens removed from machine at 10:00
	12:00		7.7	32°C		Specimens returned to machine at 12:05
FRIDAY						
17/05/02	12:00	7.6		33°C	10mV	Specimens removed from machine at 12:00
	14:00		7.6	32°C		Specimens returned to machine at 14:05
SATURDAY						
18/05/02	11:30	7.6		32°C	10mV	Specimens removed from machine at 11:35
	12:15		7.6	32°C		Specimens returned to machine at 12:20
SUNDAY						
19/05/02	11:00	7.7		34°C	10mV	Specimens removed from machine at 11:00
	12:15		7.6	32°C		Specimens returned to machine at 12:20
MONDAY						
20/05/02	10:00	7.6		32°C	12mV	Specimens removed from machine at 10:05
	11:15		7.6	32°C		Specimens returned to machine at 11:20
TUESDAY						
21/05/02	10:05	7.4		32°C	12mV	Specimens removed from machine at 10:15
	11:55		7.4			Specimens returned to machine at 12:00

Last sample group was removed on Wednesday, 2/05/02 at 17:00

APPENDIX H

APPENDIX I

SUBPROBLEM ONE: ULTIMATE TENSILE STRENGTHS

Oneway

ANOVA

strength

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1294757	4	323689.241	36.678	.000
Within Groups	803091.4	91	8825.181		
Total	2097848	95			

$p < 0.05$

Frequencies

Statistics

strength

N	Valid	96
	Missing	0
Mean		199.78
Median		176.50
Skewness		1.189
Std. Error of Skewness		.246

Kruskal-Wallis Test

Ranks

	weeks	N	Mean Rank
strength	1	19	48.45
	2	20	40.50
	3	20	39.30
	4	19	32.00
	5	18	85.08
	Total	96	

Test Statistics[a,b]

	strength
Chi-Square	41.544
df	4
Asymp. Sig.	.000

a. Kruskal Wallis Test

b. Grouping Variable: weeks

$p < 0.05$

APPENDIX J