The Application of Electro-Etching in the Manufacturing Process for Cardiovascular Stents

Vladimir Mardirosevici

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Supervisor: Mr. Gerard O'Donnell

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ABSTRACT

The objective of this project is to investigate and develop suitable surface treatment methods applicable to bio-medical devices. In particular, attention is focused on incorporating the electro-etching procedure into the manufacturing process for cardiovascular stents. The project aims to replace the currently preferred chemical etching procedure with electro-etching. At present, the surface treatment processes incorporates: chemical etching followed by ultrasonic agitation in a purified water bath, and by electro-polishing.

The Taguchi Method is applied to identify the optimum parameter settings in the electro-etching process. These parameters include: time, temperature, potential difference between electrodes, acidity level of electrolyte and the amount of agitation applied to the electrolyte by stirring. The experimental equipment employed to determine the optimum electro-etching parameters include: low-noise DC power supply, fumehood, electro-etching unit with electrodes and ultrasonic bath.

The optimised electro-etching process has been incorporated into a manufacturing production line with great success. The overall duration of ultrasonic agitation during the entire manufacturing process of stents is decreased by 37% using the electro-etching. Exposure to ultrasonic waves decreases the subsequent fatigue life of the delivered product. Therefore the reduction in exposure to ultrasonic waves by 83.3% is of considerably benefit.

A comparison study between the surface finish obtained using the chemical and the new electro-etching processes has been completed using Scanning Electron Microscope and Atomic Force Microscope. This study shows dimensional variation of ±0.00559 mm between struts thicknesses of stents treated by the two methods, while similar roughness values ($Ra=0.23\mu m$) are computed. The electro-etched stents have passed all visual and dimensional inspection procedures.

The research presented in this thesis clearly demonstrates and quantifies that the electro-etching process generates similar surface finish to the chemical process of etching.

“The trees that are slow to grow bear the best fruit.”
MOLIÉRE

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Chapter 1

General Introduction

1.1. Project Outline

The work presented in this thesis has been carried out and submitted in satisfaction of the requirements for the Master of Engineering Science at the HETAC (Higher Education and Training Awards Council). The development of novel electrochemistry techniques for a medical device is presented with the title “The Application of Electro-Etching in the Manufacturing Process for Cardiovascular Stents”.

Currently, electropolishing is the principal method of surface finishing employed in the stent manufacturing industry. Very little work has been published on the optimisation of the process for stent polishing or indeed investigation into other suitable processes. Some stent manufacturers have attempted to investigate electropolishing, but this is very much proprietary work and is not available in the public domain.

The overall objective of the project was to determine the optimum descaling treatment after the laser cutting procedure of the bio-medical devices with respect of its utilisation on implantable devices. Given the wide variety of uses of medical grade steels and the considerable differences of environments that these are subjected to, this investigation has concentrated on the use of the metal as a vascular implant, in particular vascular stents.

1.2 Overview of Thesis

In this thesis, the scientific basis of the work carried out is outlined in Chapter 2. Definitions of biomaterials and their properties are provided with emphasis being given to stainless steel, the prime material of interest for the coronary stent industry. The importance of the etching process in providing the necessary surface finishing prior to electropolishing is emphasised and the differences between electro-etching and chemical etching processes are provided.

Chapter 3 provides a very extensive literature review on both the electropolishing and passivation of stainless steel materials. Both will be described, as these are primary surface improvement techniques for stent devices. Effects of alloying and different theories explaining the advantages and disadvantages of alloying elements will be presented. Nitrogen and molybdenum alloying elements will be discussed because these two elements give a strong improvement in the stable passive film.

The novelty of the work presented in this thesis is illustrated by lack of published research in an electrochemistry method of descaling, i.e., electro-etching. Chapter 4 describes the equipment used to carry out the work presented in this thesis. The design of a custom electro-etching unit, used for experiments, is described.

Chapter 5 describes some experiments carried out on coupons of 316L steel and subsequently on 316L stainless steel stents. Design of Experiments or Taguchi evaluation method of different parameters involved in electro-etching has been employed for a better understanding of driven corrosion. The Fixture optimisation and a new alloy used in stent industry will be presented.

Chapter 6 describes the experiment and verification results and the operational qualification from electro-etching carried out on 15 mm GMIT stents.

Chapter 7 outlines the conclusions that can be made from this work and some future research recommendations are proposed.

Chapter 2

Background Information
For
Surface Finishing of Biomaterials

2.1. Introduction

Metals, biomaterials and particularly stainless steel will be presented in this chapter. The importance of passivity and ultra-finishing method of electropolishing is highlighted and explained. This chapter, as well as Chapter 4, will consider passivation and electropolishing as deliberate (selective) and controlled removal of metal in an electrolyte.

An extensive description of 316L stainless steel is presented due to its unique popularity in the Biomedical Industry.

2.2. Biomaterials

One commonly used definition of biomaterials is any material that is used to replace or restore function to a body tissue and is continuously or intermittently in contact with body fluids [1]. It is widely perceived that there will be significant advances in the development and use of biomaterials in the near future. In fact, many believe that biomaterials will soon become the dominant focus of materials research and that significant economic expansion will flow from this research. The very breadth of this field precludes a comprehensive, in-depth projection in all areas of biomaterials, which currently include orthopaedic, cardiovascular, neurological, drug delivery, and other applications [2]. Projected future applications include the use of microrobotic devices for disease detection, drug delivery, and neurological applications, for example. Gene therapy is also identified as an alternative approach to many of these same clinical problems [3].

Biomaterials science examines the mechanical, physical, and chemical properties of materials as well as the complex host responses to introduced bulk material and material surfaces, and as a discipline, is a relatively new field.

Today biomaterials help people to walk without pain using artificial joints, and people with defective hearts to lead normal live with peacemakers and artificial heart valves. It is now estimated that one in 25 people have an implant, the majority of whom have benefited from an increased length and quality of life [4].

The first requirement for any material to be placed in the body is that it should be biocompatible and not cause any adverse reaction in the body [5]. The material must withstand the body environment and not degrade to the point that it cannot function in the body as intended. For example, metals used in the cardiovascular system must be non-thrombogenic, and in general, the more electronegative the metal with respect to blood, the less thrombogenic the metal will be. This means that when it is introduced into human body, the material will exhibit a minimal response from the body. Biocompatibility is the ability of the material or device to perform in its intended function with an appropriate host response. In reality there are very few materials that satisfy these requirements. Next, the biomaterials should possess adequate physical and mechanical properties to serve as replacement or reinforcement for human body tissues.

Currently, medical device designers are limited to a relatively small number of off-the-shelf materials that were not originally designed to be used in medical implants. The development of new biomaterials requires a better understanding of the mechanisms that control cell-materials interactions. The new materials will provide both carefully tailored physico-mechanical and chemical properties as well as biologically functional interfaces with living cells. As such improved materials become available, the replacement of whole organs by synthetic substitutes becomes a real possibility.

Most biomaterials used for implants are common materials familiar to the average material engineer or scientist and Table 2.1 illustrates some of the materials commonly used in the manufacture of medical implants and devices. The materials are drawn from a number of classes, i.e. polymers, resins, natural and synthetic products, metals, ceramics, and composites. Each material and class of material has a particular combination of properties determined by its composition and production method, and each set of properties produces both benefits and limitations. Depending on the application, these materials serve as protective barriers, decorative purpose, filter membranes, load bearing members, joints, etc.

Type of material	**Specific example**
Biostable polymers and resins	Poliurethanes, silicone rubber, Teflon®, Dacron®, nylon, polymethylmethacrylate
Biodegradable polymers	Poly(lactic acid), poly(glycolic acid), polydioxanone
Natural and semi-synthetic products	Treated porcine grafts, bovine pericardium, processed cellulose, processed collagen
Metals	316 and 316L stainless steel, Vitallium®, titanium alloys, Co-Cr alloy, Co-Cr-Mo, Ti-6Al-4V
Ceramics	Aluminum oxides, calcium aluminates, titanium oxides, pyrolytic carbon, Bioglass®, hydroxyapatite
Composites	Apatite composites, carbon coated metals, carbon reinforced polymers

Table 2.1 Materials commonly used in the Manufacture of Medical Implants and Devices [7]

2.3. Stainless steels

Currently, stainless steels by definition are iron-base alloys that contain a minimum of approximately 11% chromium, the amount needed to prevent the formation of rust. Few stainless steels contain more than 30% chromium or less than 50% iron. They achieve their stainless characteristics through the formation of an invisible and adherent chromium-rich oxide surface film. This oxide forms and heals itself in the presence of oxygen. Other elements added to improve particular characteristics include nickel, molybdenum, copper, titanium, aluminium, silicon, niobium, nitrogen, sulfur, and selenium. Carbon is normally present in amounts ranging from less than 0.03% to over 1.0% in certain martensitic grades.

2.3.1. Classification of Stainless Steels

European standard EN 10088-1 presents the list of stainless steels while EN 10088 – 2 and EN 10088 – 3 describe the technical conditions for delivery of semi – finished general purpose stainless steel.

In the United States, wrought grades of stainless steels are generally designated by the American Iron and Steel Institute (AISI) numbering system, the Unified Numbering System (UNS), or the proprietary name of the alloy. In addition, designation systems have been established by most of the major industrial nations [16]. Of the two institutional numbering systems used, AISI is the older and more widely used. Most of the grades have a three-digit designation; the 200 and 300 series are generally austenitic stainless steels, whereas the 400 series are either ferritic or martensitic. Some of the grades have a one- or two-letter suffix that indicates a particular modification of the composition [17].

Stainless steels can be divided into five families. Four are based on the characteristic crystallographic structure/microstructure of the alloys in the family: ferritic, martensitic, austenitic or duplex (austenitic plus ferritic). The fifth family, the precipitation-hardenable alloys, is based on the type of heat treatment used, rather than microstructure. Figure 2.1 provides a useful summary of some of the compositional and property linkages in the stainless steel family. Table 2.2 depicts the main characteristics of these stainless steel classes.

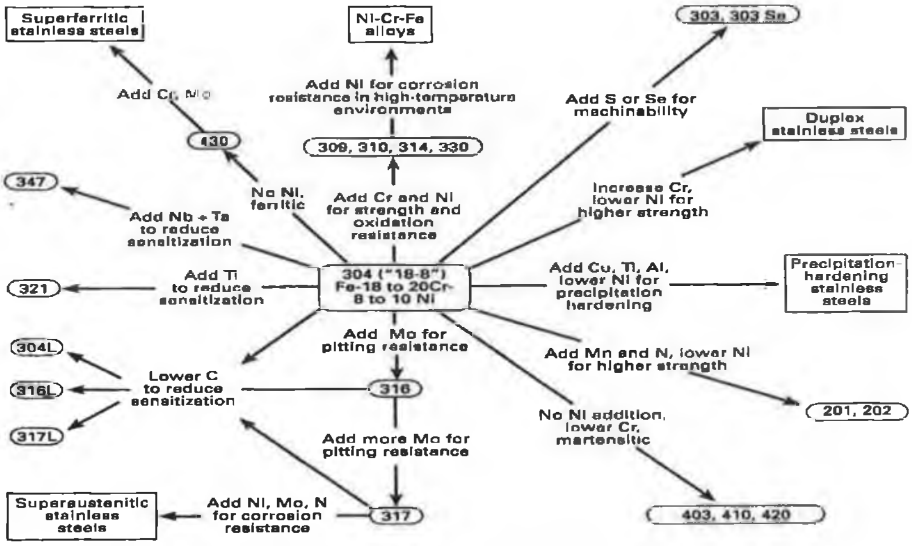


Fig. 2.1 Compositional and property linkage in the steel family of alloys [15].

Stainless steel families	**Ferritic**	**Austenitic**	**Martensitic**	**Precipitation-hardenable (PH)**	**Duplex**
Characteristics	- body centred cubic (bcc) crystal; - magnetic; - can not be hardened by heat treatment; - not high strength; - yield strength: 275 to 350 MPa; - limited fabricability; Advantages: - resistance to chlorides; stess corrosion cracking and atmospheric corrosion - 11→30% Cr; - very low carbon content	- the largest stainless steel family (number of alloys and usage); - can not be hardened by heat treatment; - not magnetic; - face-centred cubic (fcc); - excellent ductility, formability and toughness; - can be substantially hardened by cold work; - Ni is chief element used to stabilise austenite; - can be subdivided: a) chromium-nickel alloys b) chromium-manganese-nitrogen alloys c) –typical tensile yield strength 200→275MPa	- magnetic; - heat-treated structure - body-centred-tetragonal (bct); - similar to iron cast alloys that are austenised, hardened by quenching and then tempered; - in annealed condition – tensile yield strength is about 275MPa; - most commonly is AISI410; - 12%Cr; 1%C - Hardness - 20→40 HRC; - Molybdenum and Nickel ccan be added to improve corrosion and toughness proprieties.	- chromium-nickel grade that can be hardened by an aging treatment; - grades classified as austenitic, semiaustenitic or martensitic; - cold work is sometimes used to facilitate the aging reaction; - various alloying elements are used to achieve aging; - these alloys can attain high tensile stength up to 1700MPa; - good ductility and toughness; - moderate to good corrosion resistance - better combination of strength and corrosion resistance; - better combination of strength and corrosion resistance is achieved than with the austenitic alloys;	- chromium-nickel-molybdenum alloys that are blanced to contain a mixture of austenite and ferrite; - magnetic; - improved stress corrosion crack resitance compared with austenitic stainless steel, - improved toughness and ducrility compared with the ferritic stainless steel; - yield strength – 550 to 690 MPa; - original alloy in this family was predominantly ferritic; - addition of nitrogen increases the amount of austenite to nearly50%; - nitrogen improves welded corrosion proprieties, chloride corrosion resistance and toughness.

Table 2.2 Characteristics of stainless steel families

2.3.2 Selection of Stainless Steels for Biomedical Industry

The selection of stainless steel may be based on corrosion resistance, fabrication characteristics, availability, mechanical properties in specific temperature ranges, and product cost. However, corrosion resistance and mechanical proprieties are usually the most important factors in selecting a grade for a given application.

Characteristics to be considered in selecting the proper type of stainless steel for a specific application include:

- Corrosion resistance
- Resistance to oxidation and sulfidation
- Strength and ductility at ambient and service temperatures
- Suitability for intended fabrication techniques
- Suitability for intended cleaning procedures
- Stability of properties in service
- Toughness
- Resistance to abrasion and erosion
- Surface finish and/or reflexivity
- Sharpness, or retention of cutting edge
- Rigidity

While several types of stainless steels are available for implant use, in practice the most common is 316 austenitic stainless steel. The austenitic grades are used for biomedical applications as they are essentially non-magnetic which is a critical requirement.

The corrosion resistance of stainless steel can be improved by electropolishing. Another method of improving corrosion resistance is the development of a protective film by passivation of the steel [5].

In order to control microstructure and properties, a number of alloying elements are added to the basic iron-chromium, iron-chromium-carbon, and iron-chromium-nickel systems; these alloying elements include manganese, silicon, molybdenum, niobium, titanium, and nitrogen. The Schaeffler diagram (Figure 2.2) has become known as the "roadmap" of stainless steel [17].

Type 316L is used most widely in applications in which the implant is temporary, although it is also used for some permanent implants. The composition and mechanical proprieties are given in Table 2.2.

The effects of alloying are important when variations in steels are under consideration. Iron exists in two different crystal structures [18], but there are two structure transitions as the structure transforms from the high-temperature body-centred cubic (bcc) δ-ferrite at 1390 °C to the face-centred cubic (fcc) γ-austenite, which in turn transforms to bcc α-ferrite at 910 °C.

Chromium, which is the key element in the corrosion resistance of stainless steel, is a ferrite former. Carbon is an austenite stabiliser. Nickel is added to steel to stabilise the austenite phase. For 316L, the minimum combined content of these elements is 23%; the minimum chromium content is 16%, and the minimum nickel content is 7%. Molybdenum is added in amounts of 2 to 3% to strengthen the protective surface film in saline and acidic environments and to increase resistance to pitting. Molybdenum in amounts above 3% can reduce the corrosion resistance to strongly oxidizing environments and can result in the formation of some ferrite. Carbon content should not exceed 0.08%. The greatest corrosion resistance is obtained when the carbon is in solid solution and when there is a homogenous single-phase structure.

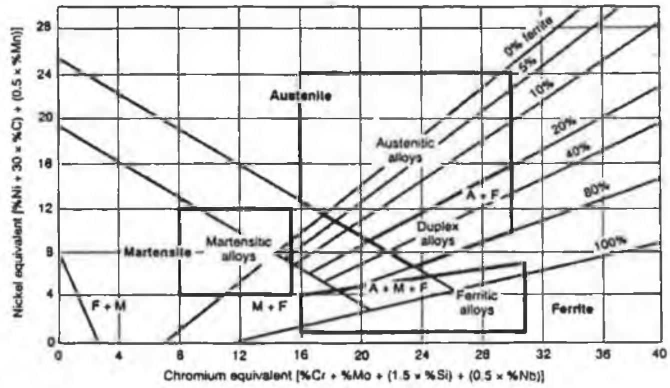


Figure 2.2 Schaeffler constitution diagram for stainless steels [17].

The corrosion resistance of stainless steels governs its continued use as an implant material. The performance of its passive layer dictates its good biocompatibility.

To broadly describe the effect of composition on microstructure in a wide range of stainless steels, the concept of chromium and nickel equivalents was developed to normalise the effect of these alloying additions on microstructural evolution, relative to the effects of chromium and nickel. Plotting the chromium and nickel equivalents on opposing axes of the Schaeffer diagram provides a graphic depiction of the relationship between composition and microstructure for stainless steels. The compositional ranges of the ferritic, martensitic, austenitic and duplex alloys have been superimposed on this diagram.

2.3.3 Physical Properties of Stainless Steel

Physical properties important for successful implementation of stainless steels include density and modulus of elasticity, thermal properties – including melting range, coefficient of thermal expansion, thermal conductivity, heat-transfer coefficient, and specific heat – magnetic properties (primarily magnetic permeability), and electrical resistivity.

Density - 7.5 to 8.0 kg/m^3.

The modulus of elasticity - The elastic modulus varies little with stainless steel composition and has values of the same order (193 GPa to 207 GPa) for all grades.

The coefficient of thermal expansion (CTE) is the change in unit of length (or volume) accompanying a unit change of temperature, at a specified temperature $\approx$17 $\mu m/m \times K$).

The heat-transfer coefficient refers to the amount of heat that passes through a unit area of a medium or system in a unit time when the temperature difference between the boundaries of the system is 1 degree – from 14.6 to 21 $W/m^2 \times K$.

Specific heat is the quantity of heat required to change by one degree the temperature of a body of material of unit mass – 460 to 500 J/kg×K.

Magnetic Proprieties. Magnetic behaviour of stainless steels varies considerably, ranging from paramagnetic (nonmagnetic) in fully austenitic grades, to hard or permanent magnetic behaviour in the hardened martensitic grades, to soft magnetic proprieties in ferritic stainless steels.

Electrical resistivity is the electrical resistance offered by a material to the flow of current, times the cross – sectional area of current flow and per unit length of current path - 600 to 800 nΩ×m.

2.4. Metals as Biomaterials

The earliest attempts at repairing the human body probably went unrecorded. There are a number of historical accounts of the development of the use of metals in the human body [8, 9]. There are a number of historical accounts of the development of the use of metals in the human body. The first record of metal implantation discusses the repair of a cleft plate with a gold plate by Petronius in 1565. In 1886, Hansmann used metal plates for internal fixation [10]. These plates, which were nickel-plated steel, had holes through which screws were inserted into the bone.

It was difficult in early times to determine whether the infection and inflammation were due to the metal of to other factors. The development of aseptic techniques by Baron Joseph Lister in the 1860s made it possible to determine the most suitable metals for use as implants. As the success of surgery increased, it became clear that the metals were an important limiting factor. The metals tested for implant use included platinum, gold, silver, lead, zinc, aluminium, copper, and magnesium [1]. All of these were found to be malleable. Magnesium was found to be very reactive in the body. Steel plates coated with gold or nickel came into use. The need for strong and corrosion-resistant metals became apparent. Stainless steels were introduced as implants in 1926, and cobalt-chromium-molybdenum-carbon alloys were first used in 1936 [11]. Titanium was determined to be inert in the body but titanium and titanium alloy were not introduced until the 1960s and came into increased use in the 1970s. Tantalum, which was studied in the early 1950s, does show some tissue reaction [12].

Biomaterials research was promoted by the founding of the Society for Biomaterials in 1974 and by increased interest among other medical and scientific societies. More emphasis was placed on standards and specifications, and the American Society for Testing and Materials (ASTM) established Committee F-4 on Medical Materials and Devices in 1964 [13].

Commonly used metallic biomaterials belong to one of the three good corrosion resistant alloy systems: iron-chromium-nickel alloys (austenitic stainless steels), titanium and its alloys as well as cobalt-chromium based alloys. Other metals that find miscellaneous uses in surgery include tantalum, some precious metal alloys such as platinum and a recent special case is the one presented by shape memory alloys. The chemical compositions and mechanical proprieties of these metals are recommended by ASTM [13] and are given in Table 2.3. This table is obtained from The American Society of Metals [5] now known as ASM International and is based on work completed by American Iron and Steel Institute.

Metals and alloys used as implants undergo an active-passive transition; therefore, corrosion resistance results from the growth of a protective surface film. These metals are in the passive state with a protective surface oxide film when used as implants and are highly corrosion resistant in saline environments. The metals currently used for surgical implants include all metals mentioned above in Table 2.2.

Metal or alloy	Chemical Composition [%]								Mechanical Proprieties			
	C	Ti	Cr	Fe	Co	Ni	Mo	Other	Yield strength [MPa]	Ultimate Tensile Strength UTS [MPa]	Elongation at Rupture A [%]	Modulus of Elasticity E [GPa]
AISI type 316 SS	0.08max	N/A	18.5	Balance	N/A	12.0	3.0	0.75Si; 0.03P; 0.03S	207	517	40	-
AISI type 316L SS	0.03	N/A	16→18	Balance	N/A	10→14	2→3	2.0Mn; 0.045P;1.0Si	$689^{1)}$	$862^{1)}$	$12^{1)}$	$200^{1)}$
Cast Co_Cr alloy	0.36max	N/A	28.5	0.75max	Balance	2.5max	6.0	1.0 max Si	450	655	8	248
Wrought Co-Cr alloy	0.15max	N/A	20.0	3.0max	Balance	2.5 max	N/A	15.3 W	379	896	-	242
Unalloyed Titanium	0.1	Balance	N/A	0.30	N/A	N/A	N/A	0.012H; 0.13O, 0.07N	$485^{2)}$	$550^{2)}$	$15^{2)}$	$110^{2)}$
Ti-6Al-4V	0.08	Balance	N/A	0.25	N/A	N/A	N/A	0.6Al; 4.0V; 0.0125H	830	895	10	124
Unalloyed Tantalum	0.01	0.01	N/A	0.01	N/A	N/A	0.01	Balance Ta, 0.001H	140→345	205→480	-	-
MP35N	N/A	N/A	20.0	N/A	35.0	35.0	10.0	N/A	240→655	795→1000	-	228

Legend:
1) AISI 316 SS cold work;
2) Titanium, grade 4;
N/A – Not Applicable

Table 2.3 Chemical composition and mechanical proprieties of metals and alloys currently used as surgical implants [6]

The metals and alloys most frequently used as implant materials will be discussed in terms of metallurgical factors and elements of alloying. For example for a better understanding is important to note that small changes in alloying additions of certain elements can result in significant changes in corrosion behaviour (see Chapter no. 3, Literature Review, section 3.2.2).

One of the most recent and significant metallic cardiovascular product is the cardiovascular stent [14], which is used to provide support to blocked blood vessels that have been opened by a balloon catheter. This product was developed in response to the limitations of balloon angioplasty, which resulted in a substantial number of repeated blockages in the same area. It is interesting to note that 316L stainless steel, whose use has diminished in orthopaedic applications, is currently widely used in cardiovascular stents. In the annealed condition its ductility can reach the flexibility and expandability required for a stent. Its excellent corrosion resistance makes it an ideal candidate material for stent devices.

All of the metallic materials used in implants fall into the category of passive metals, i.e., they owe their corrosion resistance to the presence of a stable oxide layer on their surface. These oxide layers, which form naturally, protect the metal from the corrosive environment of surrounding body fluids and tissues. The passivation layer formed on different metals contain different elements and compositions, e.g., stainless steels and Co-Cr alloys are protected by chromium oxide layer, Cr_2O_3, whereas titanium and its alloys are protected by titanium oxide layer, TiO_2. The important point about the passivity and corrosion resistance of metals is the nature of the conditions that will cause breakdown of the oxide film, which will result in corrosion. Surface passivity is an essential requirement, but surface finish can also effect performance, with highly polished surface performing better in terms of corrosion wear. Passivation of metals is discussed in detail in section 2.4, with emphasis being placed on stainless steel materials. Passivation of stent devices is enhanced by nitric acid passivation, and is an essential stage in the final processing of the device before it is sterilised and packaged.

Metals used as biomaterials must either be noble, e.g., gold, or corrosion resistant to the body environment i.e. passive. Many types of corrosion have been observed on biomaterials used in the body, including general corrosion, pitting and crevice corrosion, stress-corrosion cracking, corrosion fatigue and intergranular corrosion. Corrosion and its different forms are described fully in section 2.9. None of the above mentioned corrosion forms, with the exception of general corrosion, can be tolerated in surgical implants.

2.5. Passivation

According with Shreir et. al. [19], "passivity is a state of low corrosion rate brought about under a high anodic driving force, or potential, by the presence of an interfacial solid film, usually an oxide".

In ASTM A380 passivation is "removal of exogenous iron or iron compounds from the surface of a stainless steel by means of a chemical dissolution, most typically by a treatment with an acid solution that will remove the surface contamination but will not significantly affect the stainless steel itself". In addition, it also describes passivation as "the chemical treatment of a stainless steel with a mild oxidant, such as a nitric acid solution, for the purpose of enhancing the spontaneous formation of the protective passive film". From a manufacturing point of view, chemical passivation is attractive in terms of simplicity and being relatively inexpensive.

Some normally active metals and alloys exist that, under particular environmental conditions, lose their chemical reactivity and become essentially inert. This passive behaviour termed passivity, is displayed by chromium, iron nickel, titanium and many other alloys.

"In practical terms, the passivation process removes free-iron contamination left behind on the surface of stainless steel as a result of machining and fabricating processes. These contaminants are potential corrosion sites. It is also argued that the passivation process dissolves surface sulfides that may be present as a result of the use of alloying elements, and these inclusions can act as preferential sites for corrosion" W.M. Carrol and Howley [20].

2.6. Electro-etching

Electrochemichal etching is the deliberate (selective) and controlled removal of an electrically conducting (or semiconducting) material in an electrolyte [20].

A typical set-up for a electrochemical etching is presented in Figure 2.3. This set-up is similar with an electropolishing unit.

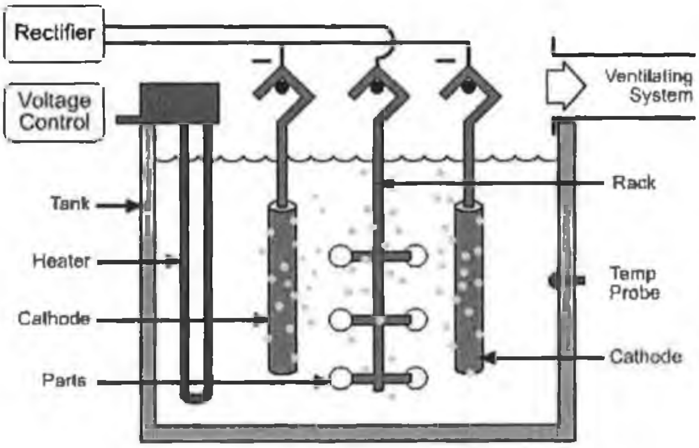


Fig. 2.3 Schematic Electro-etching Installation

The purpose for practising electrochemical etching is to control surface roughening in order to promote a better and clean surface prior to electro-polishing.

Etching of the material may be carried out either chemically under open-circuit conditions (i.e. controlled "corrosion") or it may be electrochemically driven by applying a potential. It requires no power supply or auxiliary electrodes; the electrolyte conditions are chosen such that the species to be removed is dissolved at a reasonable rate, courtesy of a simultaneous cathodic process.

Taking the case of the dissolution of a metal M, the anodic process in reaction (2.1) is supported by suitable electroreduction (2.2):

$$M - ne^{-} \rightarrow M^{n+} \qquad (2.1)$$

$$X + ne^- \rightarrow X^{n-} \qquad (2.2)$$

To give an overall etching process:

$$M + X \rightarrow M^{n+} + X^{n-} \qquad (2.3)$$

Thus, the etchant must permit active dissolution of M to Mn+ while supplying a cathodic reactant X. In the general case, both Mn+ and Xn+ may affect the rate of etching, i.e. the progress of reaction (2.3).

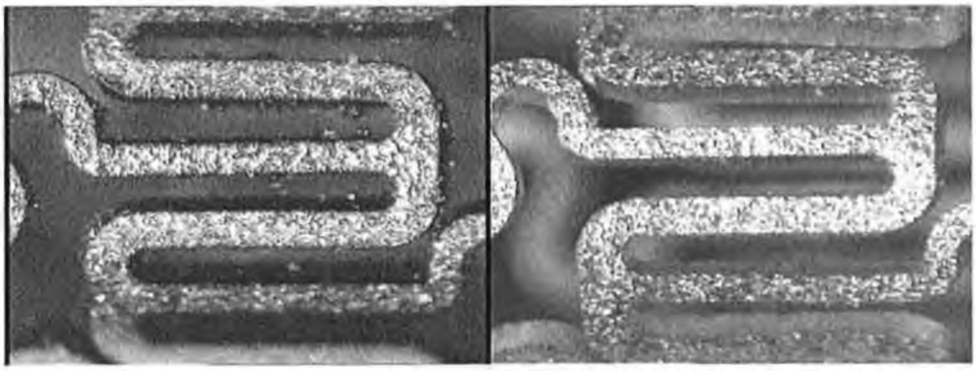


Figure 2.4 –A strut of a stent before and after etching(×50 by Microscope)

Anodic etching requires that the metal be driven to an appropiate potential (positive of its open-circuit value), by means of a power supply and a suitable inert cathode such that reaction (1) proceeds at the desired rate.

The process conditions must be chosen carefully and controlled within limits to permit the etching to be sufficiently selective both chemically and physically, e.g. it may be required to etch one metal rather than another, one metallurgical phase rather than a whole matrix or an oxide rather than a metal or semiconductor.

2.7. Electropolishing

Eletropolishing techniques utilise the anodic potential and current to aid dissolution in order to promote the polishing process. The solutions have the same basic constitution with three mechanistic requirements – oxidant (A), contaminater (B) and diffusion layer promoter (C) – but, by using anodic currents, less concentrated acid solutions can be used and an additional variable for process flexibility and control is available [19].

The electrochemical characteristics of electropolishing can be seen by referring to a typical polarisation (potential versus current density) diagram as shown in Figure. 2.5. The aim is to provide a "polishing plateau" at constant current over a substantial range of potential, but the value of that constant current can be fairly critical. Thus in Figure 2.5a the metal is passivated and in Figure 2.5c it dissolves under solution diffusion control, neither condition giving effective electropolishing.

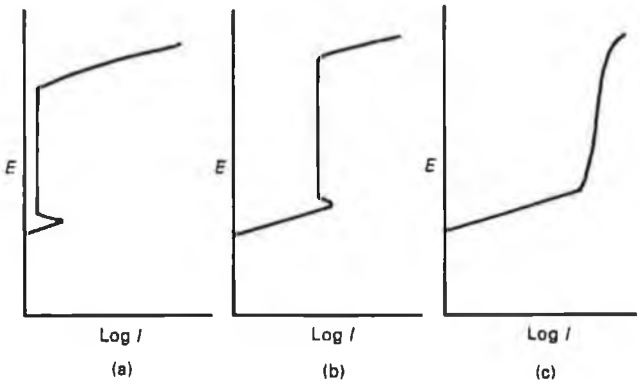


Figure 2.5 Anodic polarisation (potential-current density) curves for nickel in (a) diluted sulphuric acid, (b) cold 10 Molar sulphuric acid, and (c) hot and agitated 10 Molar sulphuric acid [19]

Referring to Figure 2.5c, the initial rise in current corresponds to simple metal dissolution and for multi-grained metals can be used to electro-etch the surface.

On a typical set-up for electropolishing the metal part to be finished is connected on anode (+) – see Figure 2.6. The Direct Current comes from Rectifier through electrical wires. The Cathode (-) may be different shaped of metallic plates.

The amount of metal removed is dependent upon: electrolyte (liquid from bath), temperature of electrolyte, time of exposure, current density and the particular alloy being electropolished.

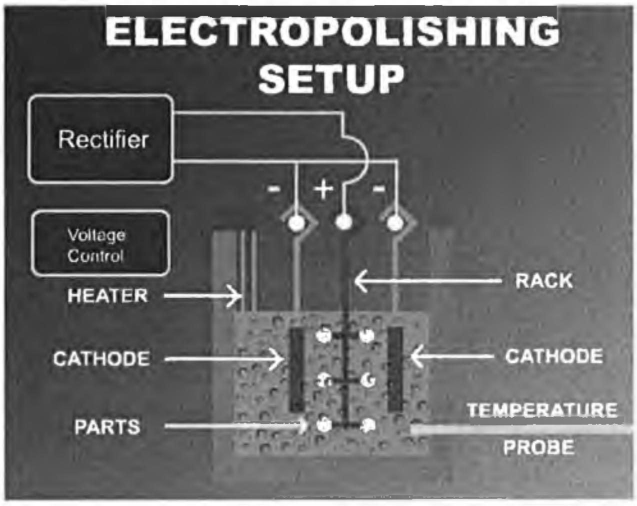


Figure 2.6 Electropolishing main set-up

Electropolishing literally dissects the metal crystal atom by atom, with rapid attack on the high current density areas and lesser attack on the low current density areas. The result is overall reduction of the surface profile with simultaneous smoothing and brightening of the metal surface. "In general, electropolishing will improve the surface finish of a part by two folds" [19]. After electropolishing any kind of scratches will be removed or attenuated (see Figure 2.7).

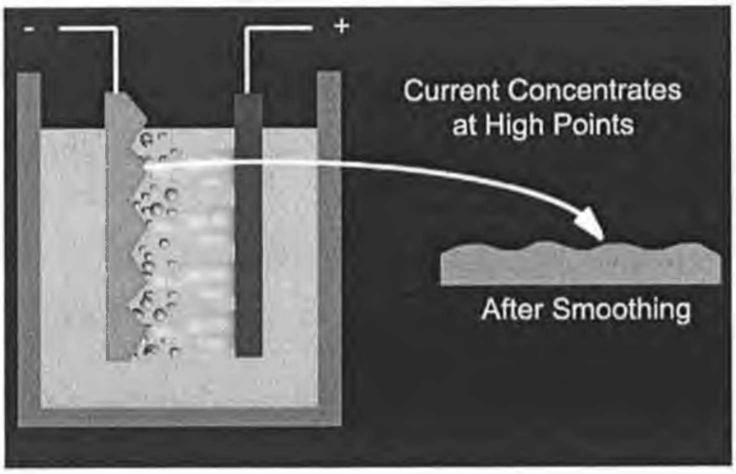


Figure 2.7 Electropolished part during and after electropolishing

The advantages of electropolishing include:

- Surface Smoothness
- Hydrogen removal
- Improving Corrosion Resistance
- Surface Brightening
- Stress Relieving

“Electropolishing is a critical surface treatment that helps assure the successful corrosion-resistant performance of stainless steels used as implant material” [21].

2.8 Electro-etching vs. Chemical Etching and Electropolishing

Several electrochemical methods are employed in the bio-medical industry because of their ability to manufacture of surface-finish metal articles, fabrications and components which are difficult or impossible to produce by traditional workshop techniques Pletcher, [24].

A less technical description of the electropolishing would be "reverse plating". Electropolishing is normally used to remove a very thin layer of material on the surface of a metal part or component. Pletcher considered that “the process is of interest because of its ability to enhance the material properties of a work piece in addition to changing its physical dimensions”.

The mechanism of electropolishing is thought to involve both selective anodic dissolution (the potential distribution will favour corrosion of the surface at peaks rather in troughs) and oxide film formation. Electropolishing leads to extremely reflective surfaces which, unlike mechanically polished surfaces, are stress-free. Before the process can be carried out successfully, however, the surface must already be smooth since macroroughness cannot be removed [24].

2.8.1 Factors involved in surface finish

Many of the factors which influence the rate of dissolution also affect the manner in which metal is removed from the anode, and hence they partly determine the surface finish. Of these factors, the anode potential and current density play a major part.

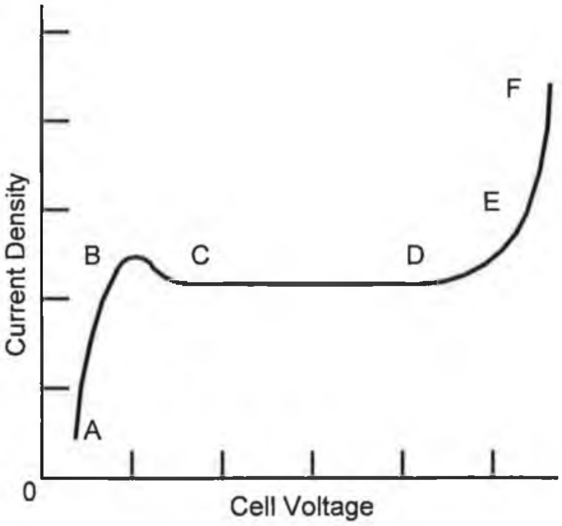


Fig.2.8 Ideal current density-cell voltage curve

In order to understand more about electro-polishing and electro-etching, plots of anode potential, cathode potential and cell voltage on current density, for different process variables, are obtained and studied. Of these, the plot of cell voltage versus current density gives more information on the critical effects of the process variables required to obtain a good polished surface. Basically, the electrolytic cell consists of the specimen anode, cathode and a suitable electrolyte that is usually agitated.

An ideal curve of cell voltage versus current density is shown in Fig. 2.8. The distinct regions of the curve are: A-B which is the region of etching, B-C is the unstable region where periodic oscillation of current is seen. C-D is the polishing region where the polishing occurs at constant current density usually called "limiting current density", D-E is the region where slow gas evolution with pitting occurs and

E-F is the region of polishing with rapid gas evolution. A study of a good polishing process involves understanding the influence of variables on the cell voltage-current density relationship, particularly on limiting current density.

Among the electro-polishing variables, some are considered as primary variables, as their influence is much more significant than those of the secondary variables mentioned. The primary variables are electrolyte temperature, stirring of electrolyte, concentration of electrolyte, surface roughness, electrode distance, polishing time, viscosity of the electrolyte and cell voltage.

The effect of the secondary variable is very small and it will not be explained in this thesis.

2.9. Stent Devices

According to Mirriam-Webster Dicrionary [22], a stent is “a short narrow metal or plastic tube that is inserted into the lumen of an anatomical vessel (as an artery or a bile duct) especially to keep a formerly blocked passageway open”. It can be considered that the stents are scaffolds which are implanted at the disease site and act to support the vascular disease and maintain an open vessel.

Stents are classified as uretral, renal, femoral artery, coronary, colonic, biliary, carotidic and duodenal according to FDA (United States Food and Drug Administration) [23]. Also a stent can be biodegradable inside human body.

The five most important mechanical characteristics of a stent are:

1. A stent must have expandability. This can also be expressed in terms of a high ratio between collapsed and expanded diameter to allow for the smallest diameter of the arterial system to be navigated.
2. The wall thickness should be as small as possible to offer the lowest profile after deployment.
3. The post implant metal surface should be as small as possible because surface area determines the degree of thrombus formation.

4. Because the degree of residual elasticity of an artery following balloon dilatation cannot be anticipated, the circumferential strength of a stent must have a wide margin of excess to prevent collapse after deployment.
5. Radiopacity is essential for precise manipulation and positioning under fluoroscopy.

2.10. Conclusion

This chapter presents information regarding biomedical materials as well as their chemical and physical properties. Also, an important part is dedicated to metals, particularly to stainless steel. Electropolishing and passivation of metals were reported as methods of enhancing biocompatibility.

Austenitic stainless steel 316L was found to be most used in biomedical industry. For this reason the finishing method of electropolishing was explained. It was considered that electropolishing increases properties of passivation for a stent. Very little work has been published on the optimisation of the process for stents polishing or indeed investigation into other suitable processes. Chapter 5 will present an optimisation method for stent descaling, which further will improve the electropolishing method of finishing.

Chapter 3

Literature Review

3.1. Introduction

This chapter presents published aspects regarding the connection between corrosion and surface finishing of steel. The overall aim of this chapter is to present the passivation and polishing of stainless steel in the current literature. In regard to the wide variety of uses of medical grade steels, this investigation has concentrated on the use of metal as vascular implant.

Electropolishing and passivation will be described considering as being the main two methods for improving surface properties of an implanted stent. Passivation will be presented in terms of its effect on corrosion resistance of the alloy. The outer layer of the metal, i.e. the oxide layer which improves passivation will be also presented. Electropolishing increases significantly the corrosion resistance of the alloy and subsequent treatments, i.e. heat treatment; seem to have a small effect on this improvement.

Effect of alloying and different theories explaining the advantages and disadvantages of different elements of alloying will be presented. Nitrogen and molybdenum alloying elements will be discussed because these two elements give a strong improvement in the stable passive film. Nitrogen is beneficial to austenitic stainless steels in that it enhances pitting resistance, retards the formation of the chromium-molybdenum phase, and strengthens the steel. There are well known synergetic properties of the nitrogen and molybdenum elements in stainless steel composition. Molybdenum is especially effective in increasing resistance to the initiation of pitting and crevice corrosion.

3.2.1. Passivation

Trepanier et. al. [25] have studied the corrosion behaviour and surface characteristics of laser-cut nitinol stents in a number of conditions, including electropolished, air aged, heat treated and passivated. The passivation was performed on electropolished stents, using a 10% nitric acid solution at room temperature. The passivated samples demonstrated superior corrosion resistance to both electropolished and heat treated samples.

As methods for evaluating corrosion resistance, Trepanier used anodic polarisation tests. The potentiodynamic experiments were carried out using a potentiostat EG&G Princeton Applied Research, model 273. The test was conducted in Hank's solution, i.e. a mixture of NaCl; $CaCl_2$; KCl; $NaHCO_3$; Glucose; $MgCl_2$ $2H_2O$; Na_2HPO_4; KH_2PO_4 ; $MgSO_4.7H_2O$. This solution was used to simulate the body fluid at 37°C.

Scanning Electron Microscopy (SEM) was used to study topography of surface treatments before and after the corrosion test. Also an Auger Electron Spectroscopy (AES) analysis was performed on samples before and after the corrosion experiment. Their AES survey spectra (100-200 eV) have been recorded from two different spots. Then, combined AES analysis and Argon ion sputter etching to evaluate the oxide layer thickness and the distributions of each element.

Results showed that electropolishing, heat treatment, air aging and nitric acid passivation of nitinol improve the corrosion behaviour of the alloy. They concluded that surface topography analyses by SEM and oxide layer thickness measurements by AES provided relations between surface physicochemical properties and corrosion behaviours. SEM micrographs indicated that the surface condition plays an important role in nitinol stent corrosion resistance.

Later O'Brien et al [26] found a passivation treatment, using 20% nitric acid at 80°C for 20 min for mechanically polished nitinol wire. A significant improvement in corrosion resistance, measured using potentiodynamic polarisation methods, has been demonstrated for both wire samples and typical stent components. Also they concluded that there are variations between different wire suppliers and different sizes, but all showed significant improvements due to the passivation. Surface analysis confirms the bulk of the oxide to be TiO_2, with some NiO. Enrichment of NiO at the outer surface is primarily evident after heat treatment but the passivation subsequently reduces this. Heat treatment does increase the oxide thickness, but subsequent passivation does not significantly change this. Improvements in corrosion behaviour after passivation are therefore primarily attributed to a reduction in the surface Ni or NiO content and an increase in the surface TiO_2 content, rather than related to oxide thickness.

Also their study showed that removal of nickel from surface has been confirmed by chemical analysis of passivation solution. The improvement in corrosion resistance appears to be proportional to the quantity of nickel removed. Upon immersion in saline solution, nickel release decreases with time, while passivation reduces the release of nickel over extended periods, when compared to heat treated surfaces. The benefit of the passivation is still evident after extended periods of immersion as demonstrated by corrosion resistance measurements.

Markworth et. al. [27] presented the main strategies for controlling the improvement of corrosion resistance of a metal surface in contact with aqueous medium. It has been proved that corrosion resistance can, in principle, be improved by imposing conditions that cause the otherwise chemically active surface to be passivated. For non-noble metals, maintenance of a state of passivation is crucial to the prevention of corrosion. Consequently, the active regime of anodic potential (i.e. that within which the metal surface is chemically active with respect to its environment) must be avoided. They use several control strategies for their investigation in order to remove a corroding metal surface from an active state and placing it in one characterized by a level of complete passivation, or at least a significantly improved level of passivation. This is accomplished with a non-linear model proposed by Sato [28] for passivation of a metal surface exposed to an aqueous environment. Markworth et. al. [27] have reported that a strategy, based on feedback control of the two-dimensional model, is shown to result in a significantly increased levels of passivation, and therefore in correspondingly improved corrosion resistance. The other two models in Sato simulation are: the classic linear feedback theory applied and an extension of the first model by addition of a third state variable. The last one is capable of yielding complete passivation. The classic linear feedback theory is shown to be unstable in the sense of passivation of a chemically active surface.

Corrosion resistance of stainless steels depends, among other parameters, on the surface state [29]. Different types of surface treatments for stainless steels have been developed to increase the corrosion resistance. Some of the treatments are: pickling, bright annealing, polishing and passivation in nitric acid. The primary aim of the surface treatments is to enhance the protective passive film by changing its composition, structure and thickness.

Several authors have studied the passivation treatments of stainless steel. The treatment improves the corrosion resistance of standard austenitic stainless steels [27; 28]. With regard to 316L stainless steel, Wallinder et. al. [29] have reported the effects of surface finish, nitric passivation and ageing in air on corrosion resistance. The methods of investigation were EIS (Electrochemical Impedance Spectroscopy), potentiodynamic polarisation measurements and XPS (X-ray Photoelectron Spectroscopy). In their study, the effect of surface finish, nitric acid passivation and ageing in air have been investigation with respect of the corrosion resistance of the material in 0.5% H_2SO_4.

The observation from EIS, potentiodynamic polarisation measurements and XPS analysis have led to the following conclusions:

- A significantly increased corrosion resistance is achieved through a nitric acid passivation treatment;
- The improved corrosion resistance can be attributed to a high Cr content in the passive film and an increased film thickness due to the passivation;

- A smooth surface finish increases the corrosion resistance;
- The effectiveness of nitric acid passivation treatment depends strongly on the nitric acid concentration, passivation time and temperature;
- The nitric acid concentration, passivation time and temperature have a larger influence on the passive film thickness than on the Cr content in the film;
- Ageing in ambient air may cause changes in the passive film and influence the corrosion resistance. Ageing after passivation leads to an increased corrosion resistance whereas before passivation has a little effect.

Although there is substantial evidence in the literature that the effect of acid treatment is positive, it is not clear what process occurs during the treatment, and the origin of the improvement of the corrosion resistance is not well established. Some authors have suggested that the improvement is the result of chromium enrichment in the passive film [30; 31], or is related to the chromium content and any other component from passive film [40]. Other authors have proposed that immersion in nitric acid removes sulphides inclusions of stainless steel and thus eliminates preferential sites for corrosion attack [32].

3.2.2. Effect of alloying elements on passivation behaviour of stainless steel

Various authors have proposed different theories explaining the advantages and disadvantages of different elements of alloying. Marcus et.al. [33] investigated the effects of nitrogen on austenitic stainless steel. There is a general consensus in the literature that nitrogen increases the corrosion resistance of molybdenum-containing austenitic stainless steels. A number of explanations have been proposed to understand these observations; the most widely recognised of which suggests that reaction of elemental nitrogen with protons at the passive film/electrolyte interface causes an increase of the local pH and, therefore, a decrease in pitting corrosion [34]. The detailed mechanism of the inhibitory effect of nitrogen on corrosion of these stainless steels is not well understood and the molybdenum in addition to nitrogen has complicated interpretation of the data. It had been proposed that there are synergistic effects between nitrogen and molybdenum that lead to an increased corrosion resistance of the molybdenum containing steels.

Protection against corrosion is in great part governed by the ability of the material to form a thin, passive layer at the alloy/electrolyte interface and XPS has been employed to probe the composition of the near-surface region of stainless steels at different stages of the corrosion process. Clayton and co-workers have used XPS to investigate passive films on molybdenum-containing austenitic stainless steels in which nitrogen has been added either via bulk addition or surface nitriding [34].

The nitrogen-containing steels were found to have improved resistance to corrosion when compared to those not containing nitrogen. It was observed with XPS that molybdenum and nitrogen were enriched in the passive films in addition to chromium, the latter which has been shown in numerous studies to be the primary alloy element found in passive films on austenitic stainless steels. The authors propose that the observed nitrogen enrichment leads to formation of a relatively stable, interstitial nitride phase at the surface of the stainless steel. In the case of the electrochemically nitrided steels, the authors suggest that active dissolution of the material is diminished due to the presence of strongly bonded, mixed interstitial nitrides which, because of their stability, act as a kinetic barrier to dissolution of the alloy and, furthermore, support a passive film containing enriched levels of molybdenum and chromium.

Kraack [35] investigated the influence of molybdenum present in stainless steel. He concluded that alloying with molybdenum led to a further improvement of the pitting corrosion resistance. The breakdown potential in 5 Molar NaCl was increased. Anodic polarisation curves in 1 Molar HCl showed that the passivation ability of the steel films increased markedly with increasing of Molybdenum content.

Both of these elements (nitrogen and molybdenum) have previously been shown to be beneficial for the formation of stable passive films on austenitic stainless steels. As discussed earlier, development of an understanding of the role of nitrogen in the corrosion behaviour of austenitic stainless steels has been impeded by the fact that the alloys investigated contain significant amounts of molybdenum and, therefore, the observed differences in corrosion from nitrogen-free steels may be due to synergistic effects between molybdenum and nitrogen in-stead of nitrogen alone.

3.2.3. Electropolishing

Electropolishing is based on the principle of anode metal dissolution in the electrolyte, described by Faraday's law. Good surface brightness and stress-free surface can be obtained by electropolishing [36]. Electropolishing streamlines the microscopic surface of a metal object by removing metal from surface of the object through an electrochemical process similar to, but the reverse of, electroplating. In electropolishing, the metal is removed ion by ion from the surface of the metal object in question.

Electrochemistry and the fundamental principles of electrolysis (Faraday's Law) replace traditional mechanical finishing techniques, including grinding, milling, blasting and buffing as the final finish. Smoothness of the metal surface is a primary and very advantageous effect of electropolishing. During the process, a film of varying thickness covers the surfaces of the metal. This film is thickest over microdepressions and thinnest over microprojections. Electrical resistance is at a minimum wherever the film is thinnest, resulting in the greatest rate of metallic dissolution. Electropolishing selectively removes microscopic high points or "peaks" much faster than the corresponding rate of attack on the corresponding micro-depressions or "valleys".

Other authors had explained electropolishing techniques that use anodic potentials and currents to aid dissolution and passivation and thus to promote the polishing process in solution akin to those used in chemical polishing.
Figure 3.1 shows two SEM pictures of an electropolished and mechanically polished nitinol surface. In general, electropolishing will improve the surface finish of a part, i.e. roughness, by two folds [37].

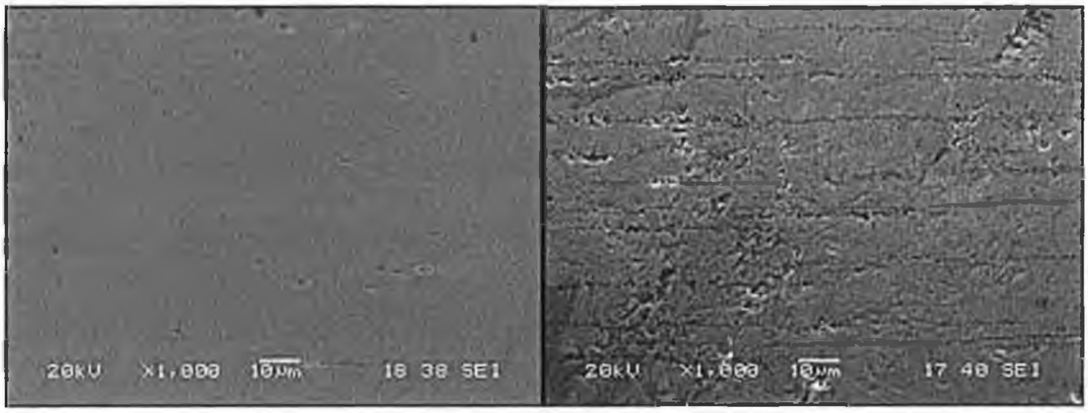


Figure 3.1 Comparison of electropolished (left) and mechanically polished (right) Nitinol (1000 magnification at SEM)

The electropolishing of stents is a well-established industrial process widely employed by the biomedical industry. One of the reason for choosing this process is that the stent is an intricate surface. However, the mechanism by which a metal surface becomes polished under anodic dissolution conditions is not clear. The original work of Jaquet [38] indicated that a "viscous" layer was formed on the metal surface during electropolishing. The occurrence of mass transfer-controlled dissolution appears to be a prerequisite for electropolishing [39], although the actual mechanisms for elimination of micro- and macro-irregularities may be different [40]. In fact, the rate of anodic dissolution appears to be entirely determined by mass transfer [41]. Their opinion is that during electropolishing a salt layer is probably present on electrode surface. In the case of nickel in sulphuric acid, an underlayer of oxide or contaminated oxide appears to exist, but more recent work on electropolishing in non-aqueous media indicates that electropolishing can be carried out in conditions where no oxide layer is present, i.e. in an active dissolution potential region [41].

It is known that the corrosion behaviour of stainless steels depends directly on the composition, structure and thickness of passive films on their surface. On this basis, it can be assumed that additional chemical, electrochemical, thermal and other treatments of stainless steel surfaces, which lead to changes of these characteristics of the natural oxide films, can affect the corrosion resistance of these materials. It is assumed that the chromium-enriched surface films formed on stainless steel can maintain the stability of the steel [42]. In respect of this it is of special interest to study the changes which occur in the chemical composition and morphology of the natural passive films on stainless steel surfaces when they are subjected to chemical and other treatments aimed to enhance the concentration of chromium and chromium oxides, respectively.

Investigations for increasing corrosion resistance were performed and described also by Stoychev et. al.[43]. They had concluded that formation of chromium-enriched surface films on the stainless steels 1.4301 and 316L as a result of chemical treatment in chromium-based solutions, alter (decrease) substantially their corrosion resistance in strongly acid media. The observed Cr^{3+} enrichment, on the one hand, and the decrease in corrosion resistance of the steels, on the other hand, permits assuming that the oxide film consists of two layers. In agreement with the bilayer model proposed by Atrens [44], the lower part of the oxide layer represents a uniform modified passive film and the upper one is a porous Cr^{3+} enriched film. This layer is an island-like structure, which permits direct attack (dissolution) of the Fe^{3+} oxides present in the lower thinner modified passive film and consequently an accelerated corrosion of the steel.

Trepanier [25] has studied the influence of different surface treatments on the corrosion resistance of Nitinol stents. Treated samples with smooth and uniform surface have a higher corrosion resistance than non treated ones which possess a very porous oxide layer. The best results of corrosion behaviour were observed for stents with the thinnest oxide layer. Similar results were obtained by Sohmura on the reliability of thin oxide for improvement of corrosion resistance of NiTi [46]. This final conclusion has important implications for the final step for fabrication of stent implants. It is proven that electropolishing increases significantly the corrosion resistance of the alloy and that subsequent treatments (heat treatment and passivation) seem to have a small effect on this improvement. Moreover, the idea of additional steps may increase the final cost of stents.

Recent theoretical results concerning the mechanism of mass-transport-limited electropolishing are summarised by Matlosz [46]. The underlying physical bases for both salt-film and acceptor models were considered with emphasis on the differences in their alternating-current impedance behaviour. Mass transport limitations for anodic dissolution are generally believed to be responsible for electropolishing, and this view is supported by the observation in numerous experimental systems of polishing for anodic dissolution along a limiting-current plateau. Levelling behaviour for anodic dissolution at the limiting current can be interpreted as the preferential dissolution of protrusions on the order of the diffusion layer due to their greater accessibility for diffuse transport. Unlike other authors such as Grimm [47], Matlosz interprets brightening of the surface as a result of mass-transport control, but on a smaller scale where diffusion is essentially isotropic and independent of the crystallographic orientation and grain structure of the metallic surface.

Whether or not anodic dissolution is mass-transport controlled depends on the experimental system. Unlike the cathodic limiting-current plateau in electrodeposition, which is the inevitable result of the depletion of metal cations in the diffusion layer near the electrode surface, anodic limiting-current plateaus do not necessarily appear with increasing overpotential in all cases since the surface concentration of dissolving metal ions will generally rise with increasing anodic current. Mass-transport-limited anodic dissolution requires therefore the presence of an additional mechanistic step, such as the precipitation of a salt film. This film limits the surface concentration to the saturation value of the metal cations.

It is of considerable scientific and technological interest to be able to determine clearly which of the possible mechanisms is at work in a given polishing system in order to understand the chemistry involved and the role of the various operating parameters. For this purpose, several studies of salt-film and acceptor systems have been undertaken in the past decade, including theoretical work on the shapes and sizes of the characteristic loops of the impedance diagrams measured along the limiting current plateau.

The two models discussed by Sohmura [45] have been studied theoretically in some detail over the past several years and represent special limiting cases of the salt-film and acceptor approaches. The first, the duplex salt-film model proposed by Grimm et al [47], attempts to characterize the role of compact and porous layers in the frequency response of complex precipitate films. The second, the adsorbate-acceptor mechanism proposed by Matlosz et. al. [48], examines the role of adsorbed intermediates and acceptor-molecule transport in the behaviour of polishing systems in the absence of films. Both types of mechanism have been observed and studied in experimental polishing systems.

Nanoscopic AFM studies concerning electropolishing stainless steel were developed by Vignal et. al. [49]. It has been shown that under certain experimental conditions, a regular network of hexagonal cells can be observed at the surface of these alloys. Its origin is tentatively attributed to an electroconvection process occurring at the metal – electrolyte interface. It is understood that in the case of stainless steel there is not much work developed at the nanoscopic scale.

For certain conditions, i.e. physical and chemical, the electropolished surface of pure metal or a metallic alloy shows particular patterns such stripes and hexagonal networks. The mechanism of formation depends on the sample/solution system considered and most of them can be not yet clarified. Stripes have been observed on electropolished samples in different conditions. Orientation and periodicity of such pattern depends on grains orientation and polishing conditions. Stripes can be obtained after crystallographic etching of stainless steel in perchloric acid based electrolytes [50].

Vignal et. al. [49] have shown that these patterns (hexagons) are observed for bath temperatures between 0 and 10°C, perchloric acid contents below 10 vol% and in absence of bath agitation. The hexagonal cells observed could be understood as prints of convective cells which would be localised in a resistive sub-layer of hundred nanometers thickness in the viscous layer [50].

It can be distinguish anodic levelling of smoothing from anodic brightening [51], as a fundamental aspect of electropolishing,. The former refers to the elimination of surface roughness of heights larger then 1µm, the latter to the elimination of surface roughness smaller than 1µm. Surface brightening thus results from the elimination of surface roughness comparable to the wave length of light. Other authors introduced the terms of macrosmoothing and brightening for anodic levelling and anodic brightening, respectively [52].

Hryniewich, [53] has reported a method for electropolishing of intricate shapes of a workpiece. In spite of good uniformity of reaction throughout the work-piece for electropolishing, there are some limitations on the quality of finish. With regards to stents, these limitations are in closed areas, i.e. places were laser beam is cutting the end parts of the struts. Hryniewich investigated the differences of current distribution in intricate areas. These theoretical and test investigations of electropolishing can suggest a conclusion that there is a big decrease in current density inside the shape. This results in particular difficulties for the uniform polishing out of the complex shape.

3.2.4. Centre of Excellence

The leading society for solid-state and electrochemical science and technology is The Electrochemical Society. This organisation has 8,000 scientists and engineers in over 75 countries worldwide who hold individual membership, as well as roughly 100 corporations and laboratories who hold contributing membership. Main publications of this society are “Electrochemical and Solid-State Letters” and “The Journal of The Electrochemical Society”. As subjects we can identify: corrosion, passivation, and anodic films; electrochemical/chemical deposition and etching as well as physical and analytical electrochemistry.

The Surface Engineering Association provides the most important aspects of surface engineering industry. The SEA bring together resources as well as technical and industrial expertise. Other related associations are: Metal Finishing Association and British Surface Treatment Suppliers Associations. Also SEA offers a complete package of activities that include: consultation with health, safety and environmental specialists at international level and links with academic institutions for education, training and new technology.

3.3. Conclusion

Corrosion resistance of the stainless steel can be attributed to high chromium content in the passive film. Passivation and electropolishing as finishing methods have been presented in different circumstances. The effect of improving fatigue through polishing was described. Surface brightening thus results from the elimination of surface roughness comparable to the wave length of light. In spite of good uniformity of reaction throughout the work-piece for electropolishing, there are some limitations on the quality of finish. In general, electropolishing will improve the surface finish of a part, i.e. roughness by two times but is in connection with quality of surface finishing.

Effects and different theories explaining the advantages and disadvantages of alloying have been presented. Molybdenum and nitrogen have been presented as elements of alloying. Both of these elements have been shown to be beneficial for the formation of stable passive films on austenitic stainless steels. There is a general consensus in the literature that nitrogen increases the corrosion resistance of molybdenum-containing austenitic stainless steels. It had been proposed that there are synergistic effects between nitrogen and molybdenum that lead to an increased corrosion resistance of the molybdenum containing steels such as 316L. It has been reported and concluded that alloying of stainless steel with molybdenum led to a further improvement of the pitting corrosion resistance. Both of these elements (nitrogen and molybdenum) have previously been shown to be beneficial for the formation of stable passive films on austenitic stainless steels.

Chapter 4

Description of Electrochemistry Equipment

4.1 Introduction

This chapter reports the experimental testing apparatus used during the course of the project. As outlined in Chapter 2 and Chapter 3, the aim of the work to be carried out in this project is to improve the process of electropolishing and cleaning of laser cut stents, i.e. etching.

4.2. Bench-top testing

All tests and experiments were performed on a bench-top provided with a fume-hood, see Figure 4.1. The fume-hood is specially designed to extract acid or any other vapours. The extraction flow can reach 1m^3/sec., but usually it was used at approximate 0.5 m^3/sec.

Figure 4.1 Bench-top layout for electrochemistry in Biomedical Industry

4.3 Electro-etching and Electropolishing

Figure 4.2 present the current manufacturing process for a stent.

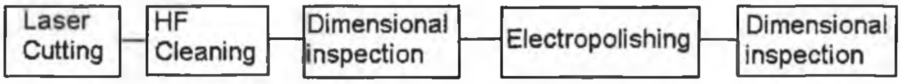


Figure4.2. Steps in current manufacturing process for stents

Currently, HF cleaning (see Figure 4.2) is run with a large amount of ultrasonic waves and usage of hydrofluoric acid.

The purpose of the electroetching process is to clean stainless steel stents. At present, after laser cutting, stents are cleaned in a solution (mixture of acid and detergent) and in ultrasonic waves. Hydrofluoric and Nitric acid solution then etches the stents. The duration of ultrasonic waves is about 30 minutes. It is believed that decreasing these waves will improve the fatigue resistance of the stents

The purpose of electrochemical etching is to control surface roughening and contamination of the entire surface in order to promote a smooth and clean surface, prior to electro-polishing.

Electro-etching (see Fig. 4.3) has been considered as an alternative to HF cleaning. It is proposed to replace the HF cleaning stage by electroetching due to its advantages.

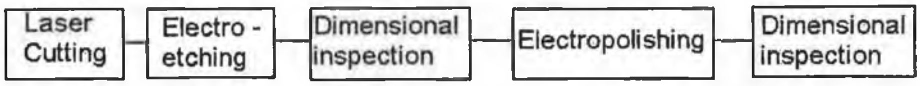


Figure 4.3 Steps in proposed manufacturing process for stents

4.3.1 Description of Electro-etching Equipment

The electro etching station consists of the following components:

4.3.1.1 Plastic stand for location of the beakers: This stand is used to accurately locate all the beakers used in the electro etching process (point 4 in Figure 4.4).

4.3.1.2 Electro etching beaker: This 1.5 litre Pyrex beaker is used to hold the electrolyte (point 1 in Figure 4.4). It also has a lid, which is acid resistant and locates the cathode (two stainless steel plates) and the anode (a copper locator/contact plate and titanium fixture).

4.3.1.3 Primary rinse bath: This 1.0 litre Pyrex beaker is used to rinse any acid drag out which may be on the titanium fixture after electro etching (point 3 in Figure 4.4).

4.3.1.4 Secondary rinse bath: This 1.5 litre Pyrex beaker is used as a secondary rinse to completely remove any remaining traces of acid and dirt (point 5 in Figure 4.4).

4.3.1.5 Ultrasonic bath: The ultrasonics are the final stage for the removal of any remaining metal by-products from laser cutting and dirt from the electro etched stents (point 6 in Figure 4.4). To do this, the stents are put in a small glass vessel that is filled with a de-ionised water and isopropyl alcohol solution.

4.3.1.6 DC power supply: This is used for delivering the desired voltage and current needed to perform the electro etching cleaning process (point 7 in Figure 4.4).

4.3.1.7 Magnetic stirring system: This is located beneath the beakers. They are used to stir the fluid in the beakers when necessary (point 2 in Figure 4.4).

4.3.1.8 <u>Heating element for electro etching beaker</u>: This heating element is used to attain a desired temperature for the electro-etching bath (point 2 and point 8 in Figure 4.4).

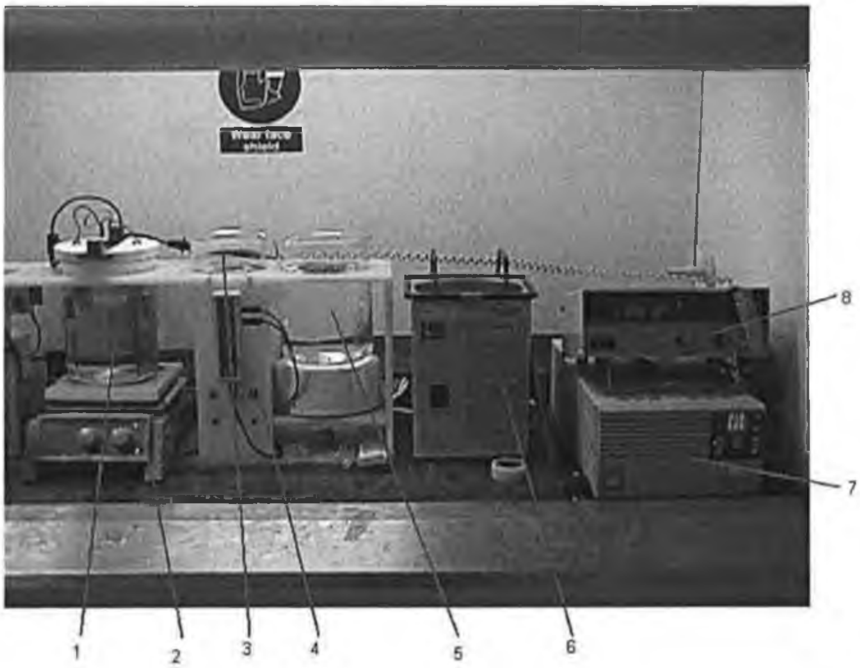


Figure 4.4 Bench-top set-up for electro-etching

In figure 4.4 the following can be identified:

1 - Electro etching beaker	5 – Secondary rinse bath
2 - Heating element for electro etching beaker	6 - Ultrasonic bath
3 - Primary rinse bath	7 - DC power supply
4 - Plastic stand	8 – Heater controller

4.4 Conclusion

This chapter presents the main components for cleaning and electropolish stents under the fumehood. A short description of their function has been given.

Chapter 5

Experimental Results

5.1 Introduction

This chapter reports experimental results performed on coupons and stents. Design of Experiments has a direct applicability in the optimisation of the cleaning process of the stents. The Taguchi method is presented for electroetching of coupons and a given stent design.

Fixture optimisation is presented as a improvement of the descaling method. A special subchapter reports the electroetching and electropolishing of a new metal used in Stent Industry.

5.2 Design of Experiment. Taguchi Method in Electro-etching

Taguchi Methods for design of experiments (DOE) were employed as quantifying method for this process. With the Taguchi approach, many statistical design efforts are simplified or eliminated. It introduces a very direct way to examine many factors at a time. Taguchi recommends the use of orthogonal arrays for constructing control factor and noise factor matrices in experimental design [54].

Coupons of 316L were used to determine the amount of mass removal involved in the electroetching process. The dimensions considered for coupons are 1mm×1mm×0.2mm. This experiment has been run three times with the same parameters.

The main key variables (factors) that were considered: time, temperature, cell voltage, concentration and stirring of electrolyte. Also investigated was the relation between (i) time and temperature and (ii) cell voltage and concentration. These parameters have been chosen because are more controllable than the other parameters and it has been assumed that these parameters have a stronger influence on the process. Table 5.1 is a array distribution of this set-up of parameters in two levels as defined by the Taguchi Method.

Exp. #	Time [s]	Temp [C]	Time×Temp	Cell Voltage [V]	Conc [M]	Cell Volt × Conc	Stirring
1	180	22.2	1	3.0	3	1	No
2	180	60.5	1	3.0	3	2	Yes
3	180	22.2	2	3.5	4	2	No
4	180	60.5	2	3.5	4	1	Yes
5	360	22.2	2	3.0	4	1	Yes
6	360	60.5	2	3.0	4	2	No
7	360	22.2	1	3.5	3	2	Yes
8	360	60.5	1	3.5	3	1	No

Table 5.1 – Parameters and levels in DOE

The results after electro-etching Taguchi experiments can be quantifying using amount of mass removal and roughness of surface.

Surface roughness was defined by ASM Handbook [55] as fine irregularities in the surface texture of a material, usually including those resulting from the inherent action of a production process. Surface roughness is usually reported as the arithmetic roughness average, Ra, and is given in micrometers see fig. 5.1.

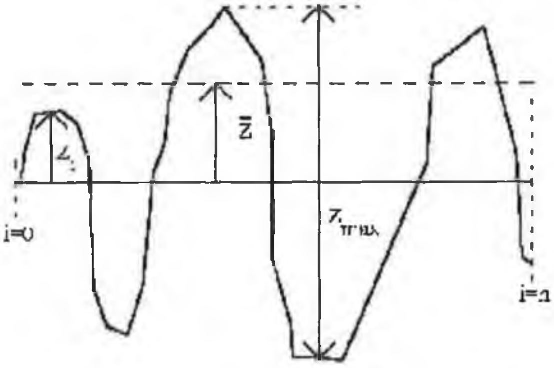


Figure 5.1 The schematic profile of a rough surface

In figure 5.1 the following can be defined:

R_a – arithmetic roughness average ($R_a = \frac{1}{N}\sum_{1}^{N}\left|Z_i - Z_{avg}\right|$); 5.1

R_q – the root mean square roughness: ($R_q = \sqrt{\frac{1}{N}\sum_{1}^{N}(Z_i - Z_{avg})^2}$) 5.2

where N is the number of measurements, Z_i is the height at position i, and Z_{avg} is the average height ($Z_{avg} = \frac{1}{N}\sum_{i=n}^{i=1} Z_i$).

The roughness and mass percentage change has been used as input data for this Taguchi experiment. The mean analysis using Anova TM – 2.0 software is shown in Graph Response for roughness (Fig. 5.2) and for mass variation (Fig. 5.3) respectively.

Table 5.2 shows the initial results of mass and surface roughness variation during the electro-etching.

Results from Atomic Force Microscopy are plotted in Appendix1.

Experim. #	m1 [g]*	m2 [g]*	Δm [g]	Δm [%]	R_a [μm]	R_q [μm]
1	0.1717	0.1636	0.0081	4.7175	0.140	0.170
	0.1608	0.1532	0.0076	4.7264	0.150	0.190
	0.1465	0.1392	0.0073	4.9829	0.160	0.220
2	0.1504	0.1354	0.0150	9.9734	0.210	0.270
	0.1554	0.1472	0.0082	5.2767	0.120	0.150
	0.1556	0.1402	0.0154	9.8972	0.160	0.210
3	0.1437	0.1218	0.0219	15.2401	0.260	0.330
	0.1447	0.1236	0.0211	14.5819	0.210	0.260
	0.1458	0.1267	0.0191	13.1001	0.270	0.330
4	0.1665	0.1223	0.0442	26.5465	0.490	0.610
	0.1541	0.1108	0.0433	28.0986	0.330	0.390
	0.1626	0.1178	0.0448	27.5523	0.360	0.440
5	0.1467	0.1279	0.0188	12.8153	0.230	0.290
	0.1529	0.1333	0.0196	12.8188	0.250	0.320
	0.1707	0.1502	0.0205	12.0094	0.270	0.330
6	0.1648	0.1410	0.0238	14.4417	0.240	0.310
	0.1676	0.1512	0.0164	9.7852	0.210	0.270
	0.1662	0.1420	0.0242	14.5608	0.330	0.420
7	0.1764	0.1252	0.0512	29.0249	0.340	0.430
	0.1683	0.1024	0.0659	39.1563	0.390	0.480
	0.1695	0.1065	0.0630	37.1681	0.390	0.480
8	0.1621	0.1014	0.0607	37.4460	0.520	0.660
	0.1593	0.0990	0.0603	37.8531	0.320	0.410
	0.1467	0.1047	0.0420	28.6299	0.280	0.350
Raw material					0.132	0.161
					0.129	0.157

*Note: Accuracy of the weight balance is ±0.0001g

Table 5.2 – Initial results from experiments (for Roughness, see Appendix 1)

were:

m_1 – initial mass of coupon; m_2 – mass after electro-etching;

Δm – mass variation ($\Delta m = m1 - m2$);

Δm [%] - mass percentage change ($m\% = \dfrac{m1 - m2}{m1} \times 100\%$);

R_a – see equation 5.1

R_q – see equation 5.2.

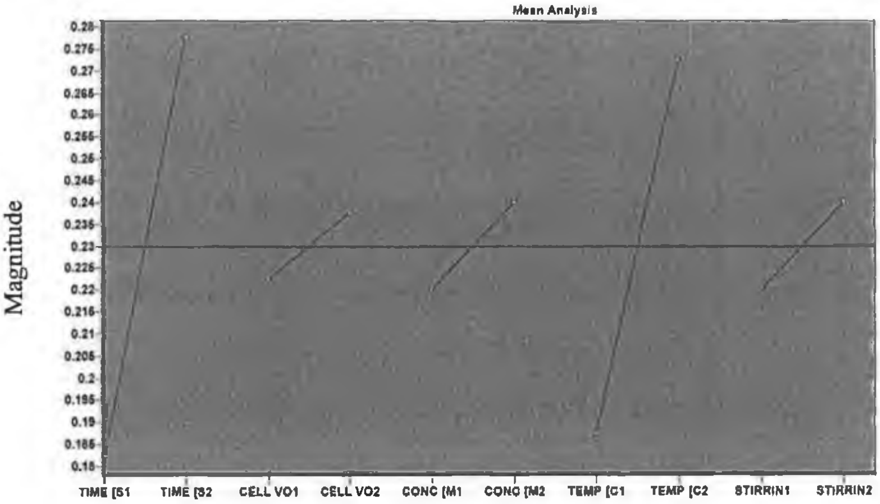


Figure 5.2 Delta Roughness Mean Analysis – from Anova - TM

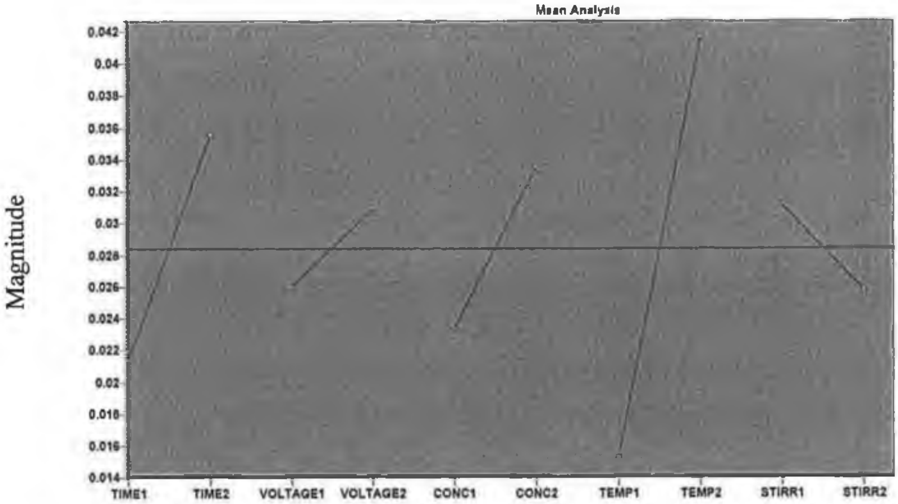


Figure 5.3 Mean Analysis of Delta mass– from Anova – TM

The Figure 5.4 shows a typical aspect of a stainless steel surface using SEM microscopy.

Figure 5.4 – Surface etched by 4 Molar at 360 seconds – 1k magnification (316L)

A cleaner surface can be achieved when there is a bigger amount of metal solved during electroetching. It can be concluded from Figure 5.2 and Figure 5.3 that the parameters are: Time2, Voltage2, Concentration2, Temperature2, Stirring1.

5.3 Experimental data of electro-etching stents

Electro-etching experiments used a set-up as shown in Figure 4.4 with a 15 mm stent defined by a pattern shown in Figure 5.5. A concentration of 3.5 Molar Sulphuric Acid was used as electrolyte. Figure 5.6 presents data on the decrease in strut thickness by increasing the time of exposure in electrolyte. This figure plots time versus physical dimensions (mm). It can be noticed that the last position (pos. 10) presents the dimensions of strut thickness after chemical descaling.

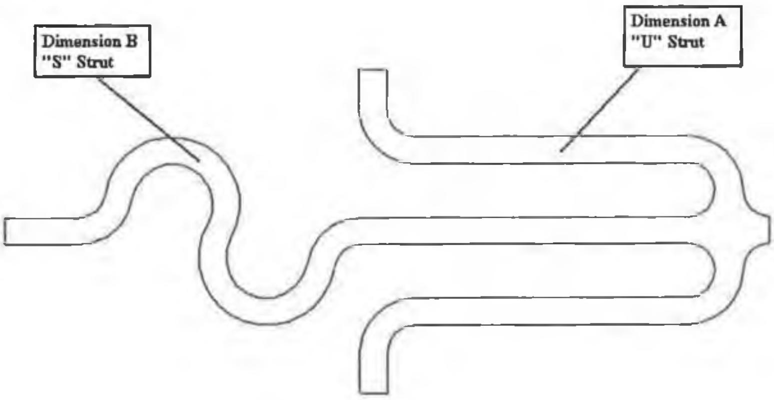


Fig 5.5 – Designed stent used for electroetching

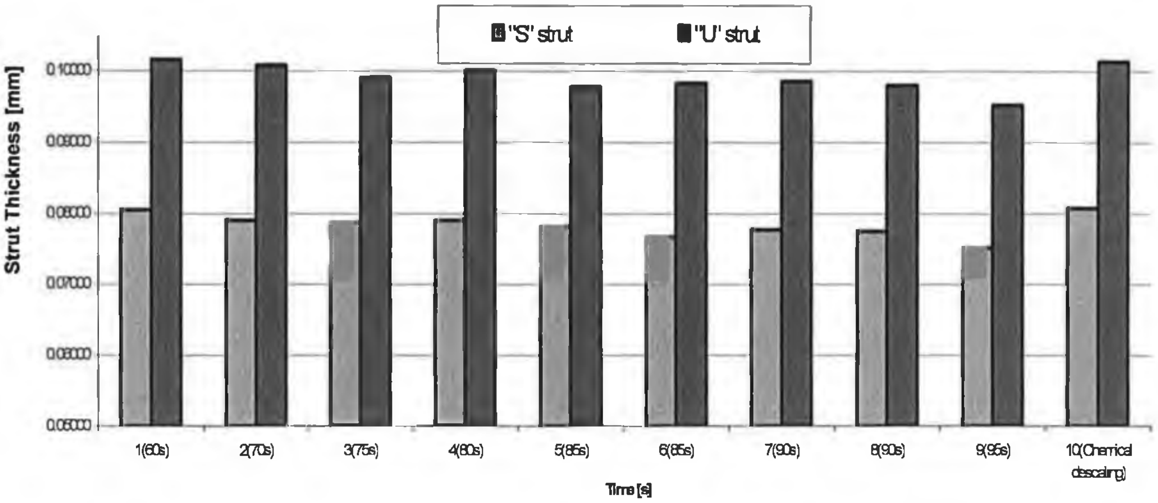


Figure 5.6 – Dimensional comparison between struts of electroetched batches (pos. 1 to 9) and HF cleaning process (pos. 10)

An acceptable compromise of stent strut dimensions within specifications, and adequate metal removal to give a clean surface, is the object of the process.

All ten experiments and results can be seen in Table 5.3. Also this table gives information about the cleaning stage of the stents.

No. Crt	Batch #	Etching Time	"S" strut		"U" strut		Obs.
			Average	Range	Average	Range	
1	2	3	4	5	6	7	8
1	LB167/11/01	60s	0.08052	0.01422	0.10160	0.01397	One of them, unacceptable, 2 very clean.
2	LB167/11/02	70s	0.07899	0.01803	0.10084	0.01346	Almost acceptable!
3	LB167/11/06	75s	0.07874	0.01397	0.09906	0.01295	Cleaned. Only one point of crud inside sur.
4	LB167/11/03	80s	0.07899	0.01829	0.10008	0.01524	Clean and acceptable! Very good!
5	LB167/11/04	85s	0.07823	0.01448	0.09779	0.01473	crud inside surface, to be repeaded
6	LB167/11/05	85s	0.07671	0.01143	0.09830	0.01803	Excellent! OK! Very clean!
7	LB167/11/10	90s	0.07772	0.01499	0.09855	0.01372	not cleaned, to be repet it
8	LB167/11/11	90s	0.07747	0.01346	0.09804	0.01346	Very clean! OK!
9	LB167/11/12	95s	0.07518	0.02057	0.09525	0.01803	Very, very clean!
10	LB167/14/13	N/A	0.08077	0.02032	0.10135	0.01676	HF etched

Table 5.3 – Etching characteristics of 15 mm GMIT stent

5.3.1 Discussion

Position 8 and 9 from Table 5.3 were passed after visual inspection and also dimensional inspection. It has been proven that there is no difference in surface quality or texture between these descaling processes. The first conclusion is that chemical etching is a step that can be easily replaced by electro-etching.

It has been proven that there are no disadvantages in the electro-etching process and that electro-etching is similar with HF cleaning without the associated loss of fatigue life.

Based on fact that electro-etching is using compatible chemicals to electropolishing it can be easily integrated in manufacturing.

5.4 Electro-etching on stents using Design of Experiment

As part of pre-validation testing a Taguchi Orthogonal array experiment was performed. This DOE was to identify the optimum settings of the main parameters and to give an overview of the influence of these parameters on the outcome of the electro-etching process. From this the optimum settings were defined.

Five parameters that are most influential on this process were used in a two level (low and high) array to analyse the process. The most suitable orthogonal array that defines this experiment was a two level L8.

The five parameters are: Temperature; Time; Voltage; Acid Concentration and Iron Content.

Expt. No.	Temperature [°C]	Time [Seconds]	Voltage [Volts]	Col.4	Acid Content [Molar]	Iron Content [g/L]	Col.7
1	25	180	3	1	3	0	1
2	25	180	3	2	4	2	2
3	25	200	3.5	1	3	2	2
4	25	200	3.5	2	4	0	1
5	35	180	3.5	1	4	0	2
6	35	180	3.5	2	3	2	1
7	35	200	3	1	4	2	1
8	35	200	3	2	3	0	2

NOTE: Column four and seven are blank.

Table 5.4 Design of Experiment for electro-etching stents

Eight experiments were carried out on stents with similar settings and the results will be detailed and confirmed in Chapter 6.

5.4.1 Pre-Validation Testing for Optimum Etch Time

The Taguchi experiment was performed on the *GMIT* stent. This gave all the optimum settings for electro etching this particular stent. Time is the only variable that needs to be adjusted to achieve clean electro-etched stents of other sizes and designs. Time is easily controlled and measured by the operator. A series of experiments were performed on each stent size at optimum operating conditions to determine an estimated optimum time for each stent size.

NOTE: The times may vary slightly depending on small variations in the acid and iron concentrations.

5.4.2 Robustness of Electro Etching Process

The optimized process is now tested for robustness to variations which may occur in a manufacturing enviroment. The parameters of time, voltage, temperature, acid content and metal content have all been identified as influential on the outcome of the electro-etching process. It has been discerned that voltage, temperature, and time are all variables that are controllable and therefore can be kept within a very close tolerance of their desired values. Acid content and iron content are more difficult to quantify, as evaporation and electrolytic drag out can alter the acid content and each batch of etched stents will increase the iron content. It is important then to ensure that the process will perform satisfactorily if there are changes in these parameters and also to determine at what stage does a variation from the target value produce an undesirable result.

To ensure the robustness of the electro-etching process, experiments will consider that will represent the worst-case scenarios in terms of deviation from the desired target value of the acid and iron content. This will consist of two experiments that are outlined in Table 5.5. Representative stents from the range of GMIT designs will be electro-etched to include the extremes in the process.

	Time	Temperature [°C]	Voltage [V]	Iron Content	Acid Content [Molar]
Experiment 1a	*	25	3	High	4.5-5.0M
Experiment 2a	*	25	3	Low	3.0-3.5M

*Determined by stent size.

Table 5.5 Set-up for worst case scenario

The stents were dimensionally inspected. Each stent was measured after electro-etching as well as after electropolishing. Visual inspection of the overall surface of the stent is required.

5.4.3 Acceptance Criteria

- The process must give equivalent results (after visual and dimensional inspection) to the HF cleaning (chemical etching) for all stents currently being processed.
- Electro-etching must give equivalent results as for stents that were HF cleaned.

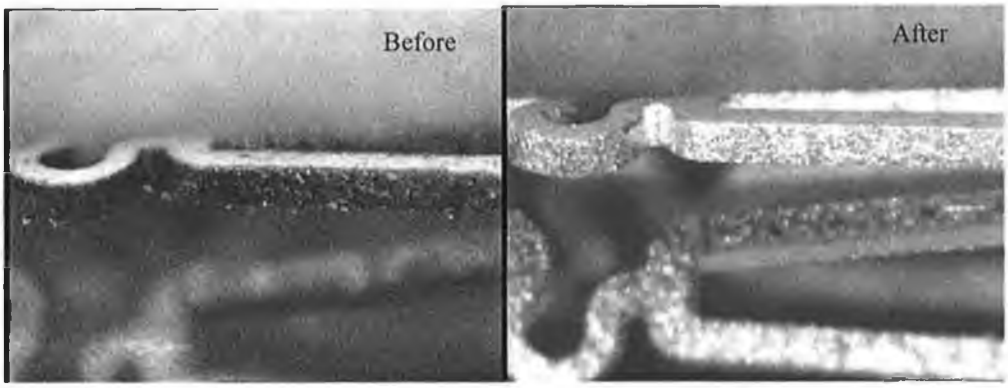


Fig. 5.7 Cut surface from a stent: before (left) and after electro-etching (×50 by Microscope)

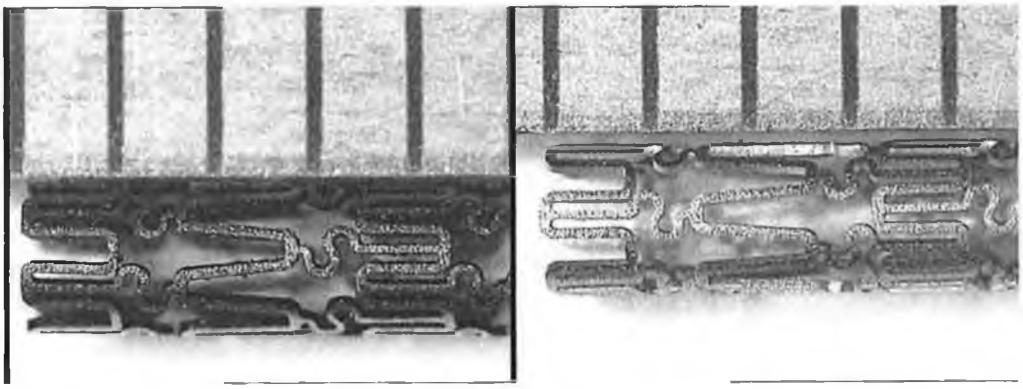


Fig. 5.8 A BiodivYsio Stent before and after electro-etching (×10 by Microscope)

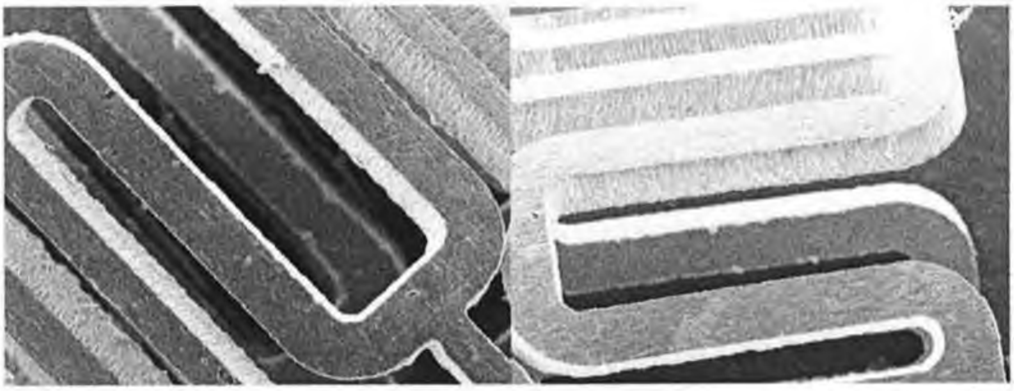


Fig. 5.9 Two views of etched surfaces on a BiodivYsio Stent (×80 by SEM)

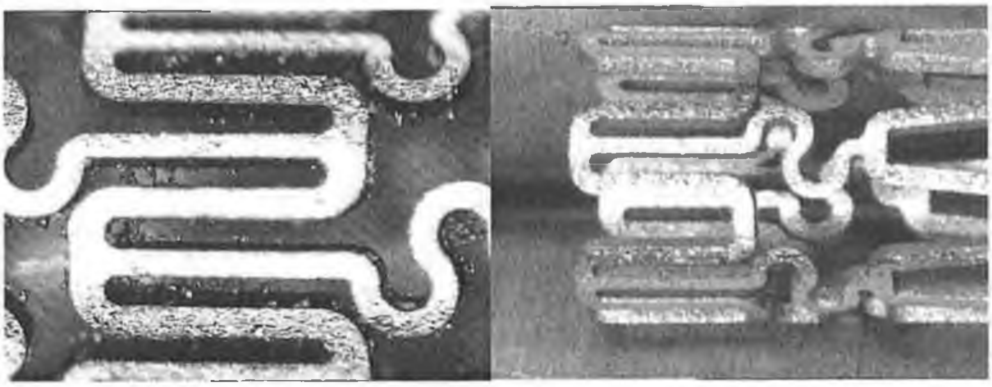


Fig. 5.10 - Struts after laser cutting (left) and struts after etching by rod

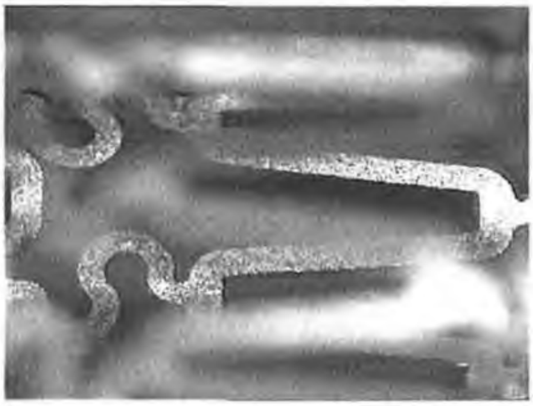


Figure 5.11 – Inner surface after etching by rod

These experiments were performed to demonstrate the robustness of the bench top electro etching process. It has been determined that of all the parameters involved in the electro-etching process, acid concentration and iron content are the ones that are most difficult to control. In light of this some experiments were run to evaluate the robustness of the electro etching process if acid content and iron content stray from their desired target values.

All parameters were left at the target values for the stents tested, except for acid and iron content. These were set to values of low and high. Setting these values at low and high mimics the worst case scenario for the electro etching process should these parameters stray from their target value.

5.4.4 Performing the Experiments

After being etched the stents were visually and dimensionally inspected. From these measurements the effectiveness of the electroetching process was established. The experiments are outlined in the Table 5.4.

5.4.5 Results

The results from the experiments can be seen in Table 5.6 for Visual Inspection and Table 5.7 for Process Capability, respectively.

Stent Size	*Visual Inspection Results**	
	High Iron and Acid	*Low Iron and Acid*
7mm	0.9 Batch # B4	0.9 Batch # B5
15mm	0.9 Batch # B3	0.9 Batch # B7
28mm	0.9 Batch # B2	0.7 Batch # B6
15mm	0.7 Batch # B1	0.7 Batch # B8

*0.0→1.0 – 1.0 being best.

Table 5.6 Visual Inspection Results

Stent Size	Process Capability (CP)	
	High Iron and Acid	*Low Iron and Acid*
7mm	* Batch # B4	* Batch # B5
15mm	1.78 Batch # B3	1.83 Batch # B7
28mm	1.46 Batch # B2	1.39 Batch # B6
15mm	1.97 Batch # B1	2.12 Batch # B8

* Not possible to measure

Table 5.7 Process Capability (C_P) Results

5.4.6 Conclusion

From visual inspection results (Table 5.6) it can be seen, even with large variations from target (in the acid and iron content) of the electro-etching process, that there is very little effect on the overall cleanliness of the stents. This is highly desirable as it shows a robust process that will perform well even if unwanted noise (variations from target values of acid and iron content) is introduced.

From Table 5.6, 0.7 means that the process is acceptable and there is residue in less than three areas that will be removed during the electropolishing process.

Also the high C_P - Process Capability - value (Table 5.7) that has been obtained from measuring the stents on the an automated dimensional inspection system has confirmed that the process is robust. Even large variations in the acid and iron content does not lead to a drastic deterioration in the stent dimensions after electro-etching.

It can be concluded that the daily testing of the electrolyte for acid and iron content for the electro etching baths, will keep the process running efficiently without any concern of poorly cleaned stents or removal of excess metal from the struts.

5.5 Fixture Optimisation

It is widely known within the industry that the design of a new type of hook for holding the stent will improve overall process of descaling and electropolishing. In the biomedical industry hooks are a special fixture made to have good electrical contact between anode and stent. Their function is to keep a good and strong contact between anode and objects to be polished. Also these wires are designed to keep the stent in position. Commonly used materials for hooks are Nickel, Nitinol, Platinum and Titanium. Normal hooks are simple loops of wire. It was decided to design a new shape with more uniform spread of current in the entire volume of stent. After evaluating different geometries the helical shape was eventually selected (see Figure 5.12). After a given number of usages Nitinol wire becomes pitted as shown in the right part of Figure 5.12.

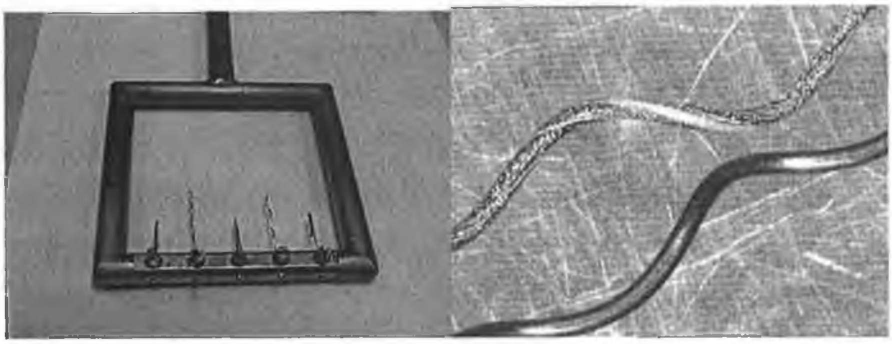


Figure 5.12 Helix hook optimisation (Nitinol wire). Pitted and new hook (right picture)

Other hook shapes were made from wire in square and "v" shape (see figure 5.13). Also a solid square design was investigated.

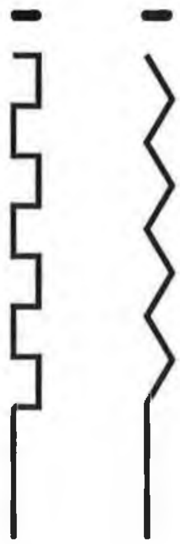


Figure 5.13 Different shapes used in hook optimisation

To achieve a uniform process, electropolishing with hooks is performed by rotating the stent upside-down at the middle of the process. This operation of rotation can be avoided if the shape of the hook is in contact along the entire inside surface of the stent.

A solid rod of titanium was adopted because this metal does not interact in the etching and electropolishing bath. Also, a uniform spread of current along the entire stent was considered. Table 5.8 shows the differences the between bottom and top of the main components for a particular stent design.

Bottom-Top Comparison of electro-etched stent (on steel rod)												
	Average						Range					
Crt no.	Symmetrical S [in]		Flat [in]		Arrow [in]		Symmetrical S [in]		Flat [in]		Arrow [in]	
	Bottom	**Top**	**Bottom**	**Top**	**Bottom**	**Top**	**Bottom**	**Top**	**Bottom**	**Top**	**Bottom**	**Top**
1	0.00290	0.00293	0.00375	0.00375	0.00382	0.00377	0.00053	0.00055	0.00046	0.00045	0.00045	0.00066
2	0.00303	0.00295	0.00386	0.00380	0.00388	0.00383	0.00050	0.00065	0.00055	0.00050	0.00054	0.00046
3	0.00318	0.00308	0.00395	0.00390	0.00405	0.00396	0.00044	0.00035	0.00041	0.00041	0.00044	0.00049
4	0.00291	0.00295	0.00374	0.00370	0.00382	0.00377	0.00057	0.00063	0.00045	0.00039	0.00059	0.00056
5	0.00296	0.00297	0.00378	0.00376	0.00384	0.00383	0.00043	0.00050	0.00045	0.00057	0.00055	0.00057

Table 5.8 – Dimensional comparison between strut thicknesses

This table shows a comparison between one side (bottom) and the other side (top) thickness of strut dimensions, i.e. Symmetrical S, Flat and Arrow. It can be concluded that there is no major dimensional difference along the stent.

5.6 New Alloys Used in Stent Industry

L-605 is a corrosion- and heat-resistant Co-Cr-W alloy whose original application was in gas turbines components such as blades, rotors, combustion chambers, and afterburner parts [56] and [57]. It is frequently used in the annealed condition, but can be hardened by cold working and suitable aging treatments. At ambient temperatures, L-605 has good corrosion resistance to marine environments, acids and body fluids. This corrosion resistance makes L-605 an attractive material for some biomedical components.

The published literature on the manufacture of L-605 for cardiovascular stents appears limited though it is known that L-605 is in use for stent applications. Other niche biomedical applications for L-605 include heart valves and bone drill bits.

Here will be presented some Scanning Electron Microscopy images with different magnifications of the electropolished L-605 stents. Polished surface and mirror aspect can be observed also using a visual microscope (see Figure 5.14). As reference it was shown in Figure 5.15 a polished stainless steel stent.

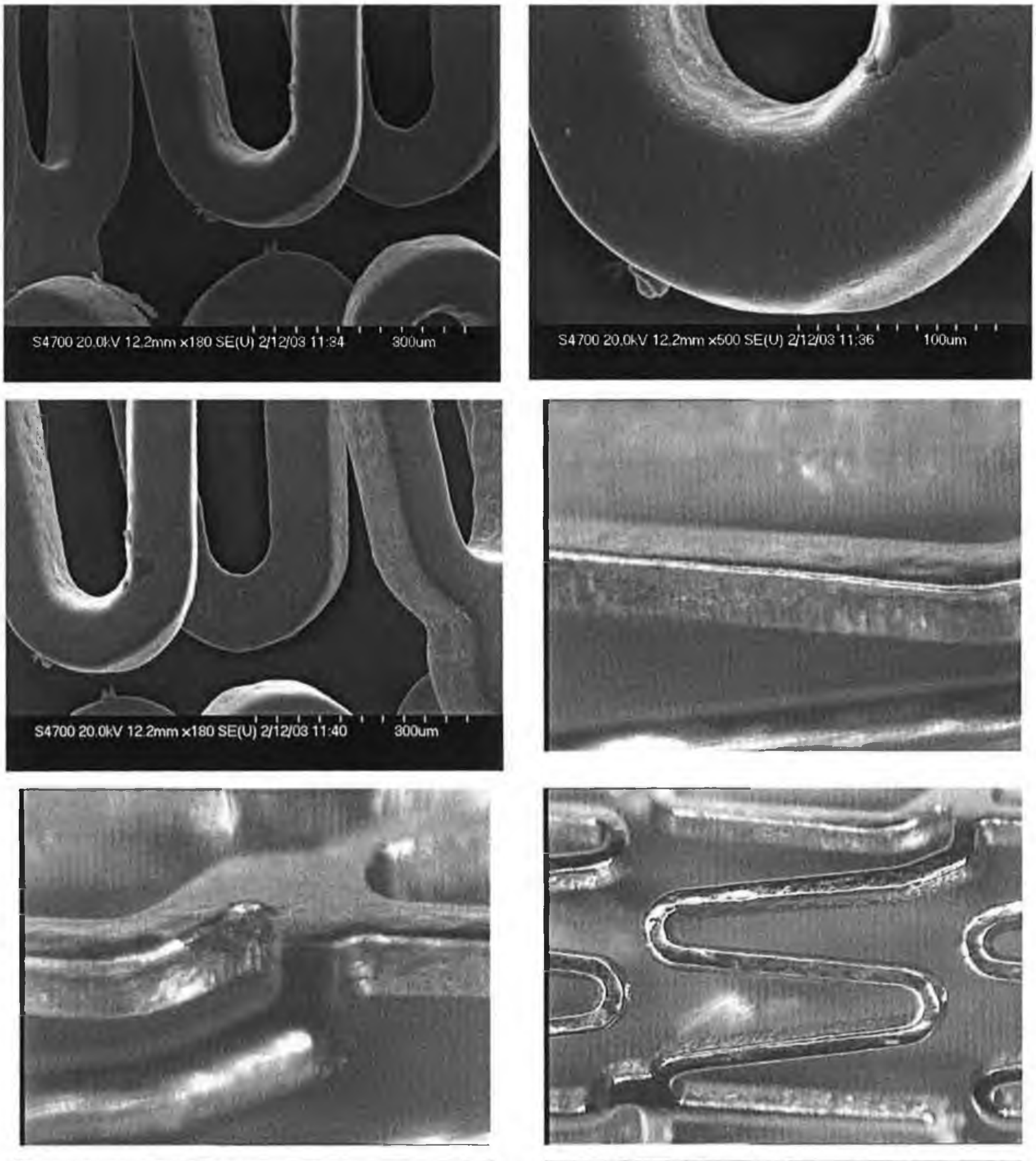


Figure 5.14 – Different parameters of electropolishing on L605 stents (SEM and Microscope)

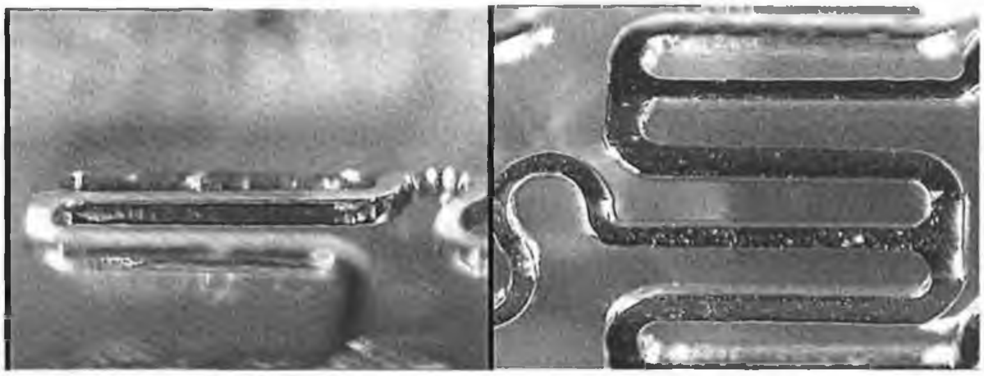


Fig 5.15 Electropolished surfaces of a 316L BiodivYsio design(×80 magnification)

Areas of investigation to consider are:

- Formation and depth of heat affected zones during laser cutting.
- Changes in microstructure due to the thermal expansion experienced, for example dissolution and precipitation of carbides or other phases.
- If a heat affected zone is formed, is it removed by electro-polishing?
- What are the optimum electropolishing parameters for achieving the desired surface finish and surface microstructure?

Various recipes for electropolishing of cobalt alloys exist. The chemicals from the open literature tend to be those used for metallography, rather than commercial electropolishing of components. For cobalt superalloys, one recommended recipe is [57]: 900 ml distilled H_2O; 100 ml H_2SO_4 (95-97%); 4-6 V DC; time from seconds to minutes with a stainless steel cathode.

5.6.1 Conclusion

Work carried out for electropolishing cobalt-base alloy L605 was also presented. It is believed that this alloy with its proprieties of corrosion and radiopacity could represent a future alternative to actual 316L Stainless Steel.

5.7 Conclusion

Bench-top testing of electro-etching and Electrochemistry set-up for Biomedical Industry was presented. Experiments on coupons and GMIT stent design were carried out for surface finishing improvement. Parameters and their influence in achieving a better surface finishing were discussed.

Electro-etching was presented as a cleaning method for 316L Stainless Steel. It was found that chemical etching easily could be replaced by electro-etching as a method of cleaning. This replacement can be a good step forward for a future integrated unit of stent manufacturing (from laser-cut stent to electro-polishing).

Chapter 6

Operational Qualification
for
Manufacturing Environment

6.1 Introduction

As part of the Operational Qualification, a Taguchi orthogonal array experiment was performed. This DOE will identify the optimum settings of the main parameters and will give an overview of the influence of these parameters on the outcome of the electro-etching process. The optimum settings will be defined. Process capability (C_p) factor will prove that the process of electro-etching is reliable.

6.2 Background experiment

This experiment has been run three times with the same parameters. The main key variables that were considered were: time, temperature, cell voltage, concentration and iron content of electrolyte. At the same time it has been assumed that there are interactions between parameters such as time and temperature; cell voltage and concentration. These parameters have been chosen because they are more controllable then other parameters and it has been assumed that these parameters have a stronger influence on the process. Table 6.2 is a array distribution of this set-up of parameters in two levels as defined by the Taguchi Method. The DOE was performed to identify the optimum setting of the most influential factors involved in the electro etching process.

These factors were identified as:

- Temperature
- Cell Voltage

- Iron Content
- Acid Concentration
- Time

A two level L8 Orthogonal Array was chosen as the most suitable matrix to fully capture the experimental space (Table 6.1).

Expt. No.	Temperature [°C]	Time [Seconds]	Voltage [Volts]	Col.4	Acid Content [Molar]	Metal Content [g/L]	Col.7
1	25	180	3	1	3	0	1
2	25	180	3	2	4	2	2
3	25	200	3.5	1	3	2	2
4	25	200	3.5	2	4	0	1
5	35	180	3.5	1	4	0	2
6	35	180	3.5	2	3	2	1
7	35	200	3	1	4	2	1
8	35	200	3	2	3	0	2

Table 6.1 Two Level L8 Orthogonal Array

The experiments consisted of running a batch of five stents to the factors settings dictated by the L8 Orthogonal Array. There were 8 experiments in total. The methods used to identify the results of each experiment on the stents was as follows:

- Stent mass before and after electro etching.
- Stent inspected on the Smartscope (Dimensional inspection machine).
- Visually inspected all five stents after each experiment.

Weighing of the stents determined the amount of metal removal per experiment. The greater the amount of metal removed the cleaner the stents but conversely, a large amount of metal removal can reduce strut dimensions below acceptable limits. An acceptable compromise of stent strut dimensions within specifications, and adequate metal removal to give a clean surface, is the object of the process. Results of mass removal can be seen in Table 6.2.

Inspection on the Smartscope accurately recorded the stent dimensions. As stated above, the strut dimensions need to be within a certain subassembly spectrum. C_P (Process Capability) will be used to determine which of the experiments is most efficient. An acceptable result is one that is in statistical control and whose output falls within the upper specification limits and the lower specification limits. The larger the C_P value the better the process. Results for this can be seen in Table 6.3.

All stents were visually inspected to ensure that they have the desired cleanliness after the electro etching process. Defects such as pitting, high metal removal rates and burnt struts were also recorded. Observations from the visual inspection were rated from 0.0→1.0 (1.0 being best). This rating was also used to determine which of the experiments was most efficient. These results can be seen in Table 6.4.

6.3 Results

The results of the different procedures used to measure the outcome that the experiments have on the etched stents can be seen in the following tables.

These results are used to determine which of the factors are most influential on the electro etching process and also what setting of these factors will achieve the best-cleaned stent.

	Exp 1	**Exp 2**	**Exp 3**	**Exp 4**	**Exp 5**	**Exp 6**	**Exp 7**	**Exp 8**
Run 1								
Mass before etching [g]	0.1032	0.0998	0.1021	0.1	0.1046	0.0904	0.0993	0.1022
Mass after etching [g]	0.0767	0.0769	0.073	0.0775	0.074	0.0465	0.0725	0.0805
Difference [g]	0.0265	0.0229	0.0291	0.0225	0.0306	0.0439	0.0268	0.0217
Run 2								
Mass before etching [g]	0.0997	0.0997	0.0982	0.1007	0.0997	0.093	0.0994	0.1016
Mass after etching [g]	0.078	0.0852	0.0662	0.0863	0.0683	0.0568	0.07	0.0717
Difference [g]	0.0217	0.0145	0.032	0.0144	0.0314	0.0362	0.0294	0.0299
Run 3								
Mass before etching [g]	0.1057	0.0987	0.0994	0.1015	0.1026	0.0905	0.1002	0.1067
Mass after etching [g]	0.0826	0.0794	0.0719	0.0763	0.0821	0.0516	0.0743	0.0718
Difference [g]	0.0231	0.0193	0.0275	0.0252	0.0205	0.0389	0.0259	0.0349
Average Difference [g]	0.023766	0.0189	0.029533	0.0207	0.0275	0.03966	0.027366	0.028833

Table 6.2 Mass removal on different runs [g]

Process Capability (C_P)

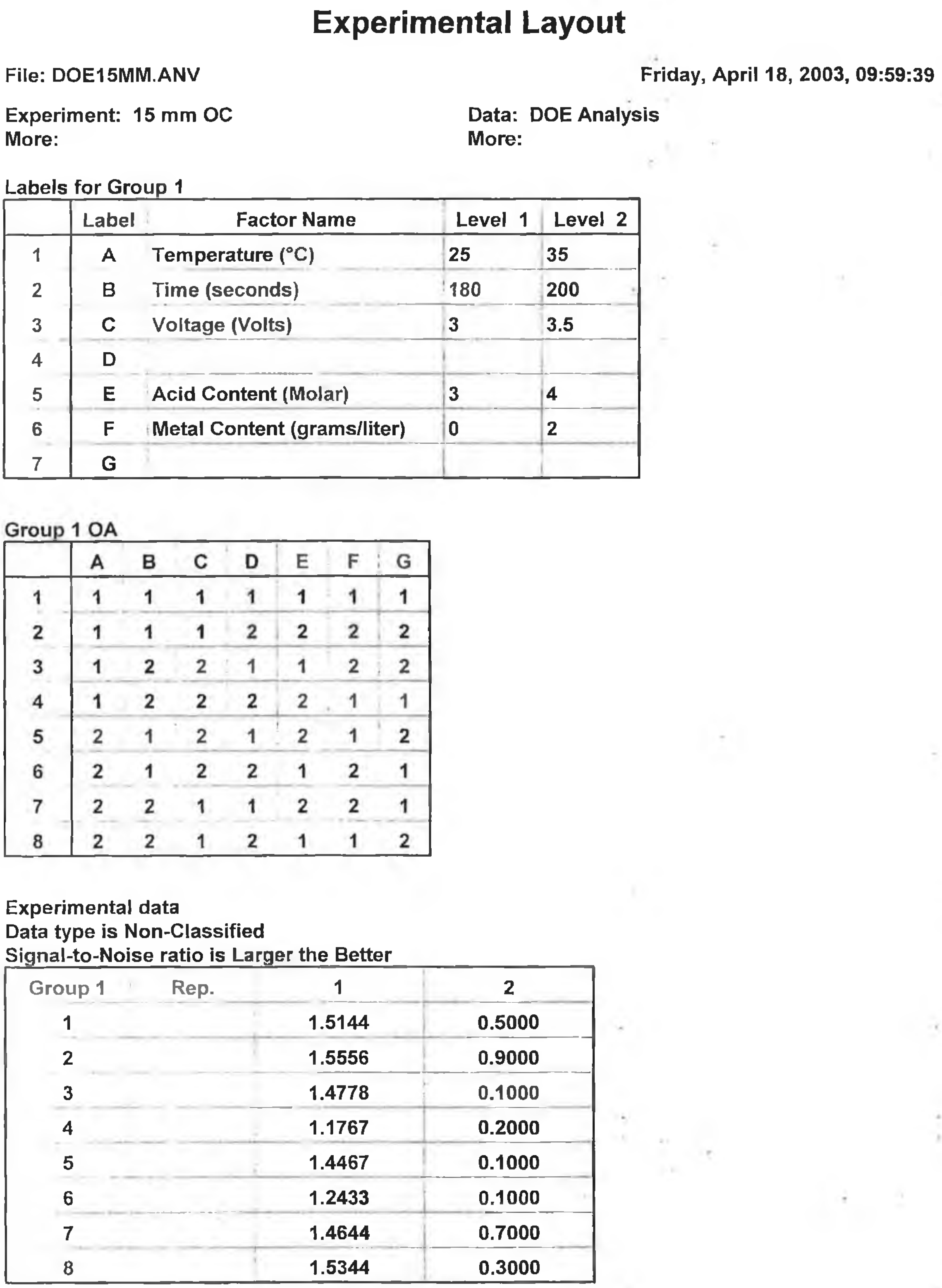
	Run 1	Run 2	Run 3	Average
Experiment 1				
Symmetrical S	1.81	1.73	1.57	1.703333
Flat	1.51	1.84	1.37	1.573333
Arrow	1.32	1.18	1.3	1.266667
				1.514444
Experiment 2				
Symmetrical S	1.63	1.86	1.64	1.71
Flat	1.56	1.66	1.72	1.646667
Arrow	1.28	1.33	1.32	1.31
				1.555556
Experiment 3				
Symmetrical S	1.48	1.4	1.9	1.593333
Flat	1.5	1.54	1.73	1.59
Arrow	1.21	1.26	1.28	1.25
				1.477778
Experiment 4				
Symmetrical S	1.13	1.22	1.53	1.293333
Flat	0.97	1.26	1.14	1.123333
Arrow	1.32	1.06	0.96	1.113333
				1.176667
Experiment 5				
Symmetrical S	1.64	1.65	1.6	1.63
Flat	1.46	1.46	1.6	1.506667
Arrow	1.19	1.14	1.28	1.203333
				1.446667
Experiment 6				
Symmetrical S	1.3	1.38	1.11	1.263333
Flat	1.17	1.19	1.31	1.223333
Arrow	1.16	1.22	1.35	1.243333
				1.243333
Experiment 7				
Symmetrical S	1.78	1.5	1.54	1.606667
Flat	1.6	1.41	1.56	1.523333
Arrow	1.24	1.25	1.3	1.263333
				1.464444
Experiment 8				
Symmetrical S	1.71	1.73	1.62	1.686667
Flat	1.46	1.6	1.53	1.53
Arrow	1.37	1.38	1.41	1.386667
				1.534444

Table 6.3 Smartscope results for Process Capability (C_P)

	Run No	**Pitting**	**Burnt Struts**	**Δm [%]**	**Average Δm [%]**	**Excess Metal Removal**	**Comment**	**Rating***
Exp 1	*Run 1*	No	No	25.68	23.10	Yes	Clean Stents. A little too much metal removed.	0.5
	Run 2			21.77				
	Run 3			21.85				
Exp 2	*Run 1*	No	No	22.95	19.01	No	Clean Stents. Good Result	0.9
	Run 2			14.54				
	Run 3			19.55				
Exp3	*Run 1*	Yes	Yes	28.50	29.58	Yes	One burnt stent and quite a lot of pitting and metal removal.	0.1
	Run 2			32.59				
	Run 3			27.67				
Exp 4	*Run 1*	Yes	No	22.50	20.54	No	Pitting on these Stents	0.2
	Run 2			14.30				
	Run 3			24.83				
Exp 5	*Run 1*	Yes	Yes	29.25	26.91	Yes	There was a lot of metal removal from all three runs. Struts were burnt and pitted.	0.1
	Run 2			31.49				
	Run 3			19.98				
Exp 6	*Run 1*	No	No	48.56	43.49	Yes	Too much metal removal. Bad result.	0.1
	Run 2			38.92				
	Run 3			42.98				
Exp 7	*Run 1*	No	No	26.99	28.67	Yes	Good Result. A little too much metal removal.	0.7
	Run 2			29.58				
	Run 3			29.43				
Exp 8	*Run 1*	No	No	32.71	31.62	Yes	Quite a lot of metal removal. Stents were clean. No pitting or burning of struts.	0.3
	Run 2			29.43				
	Run 3			32.71				

* Rating 0.0→1.0 (1.0 being best)

Table 6.4 Visual Inspection



Experimental Layout

File: DOE15MM.ANV
Friday, April 18, 2003, 09:59:39

Experiment: 15 mm OC
More:

Data: DOE Analysis
More:

Labels for Group 1

	Label	Factor Name	Level 1	Level 2
1	A	Temperature (°C)	25	35
2	B	Time (seconds)	180	200
3	C	Voltage (Volts)	3	3.5
4	D			
5	E	Acid Content (Molar)	3	4
6	F	Metal Content (grams/liter)	0	2
7	G			

Group 1 OA

	A	B	C	D	E	F	G
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

Experimental data
Data type is Non-Classified
Signal-to-Noise ratio is Larger the Better

Group 1	Rep.	1	2
1		1.5144	0.5000
2		1.5556	0.9000
3		1.4778	0.1000
4		1.1767	0.2000
5		1.4467	0.1000
6		1.2433	0.1000
7		1.4644	0.7000
8		1.5344	0.3000

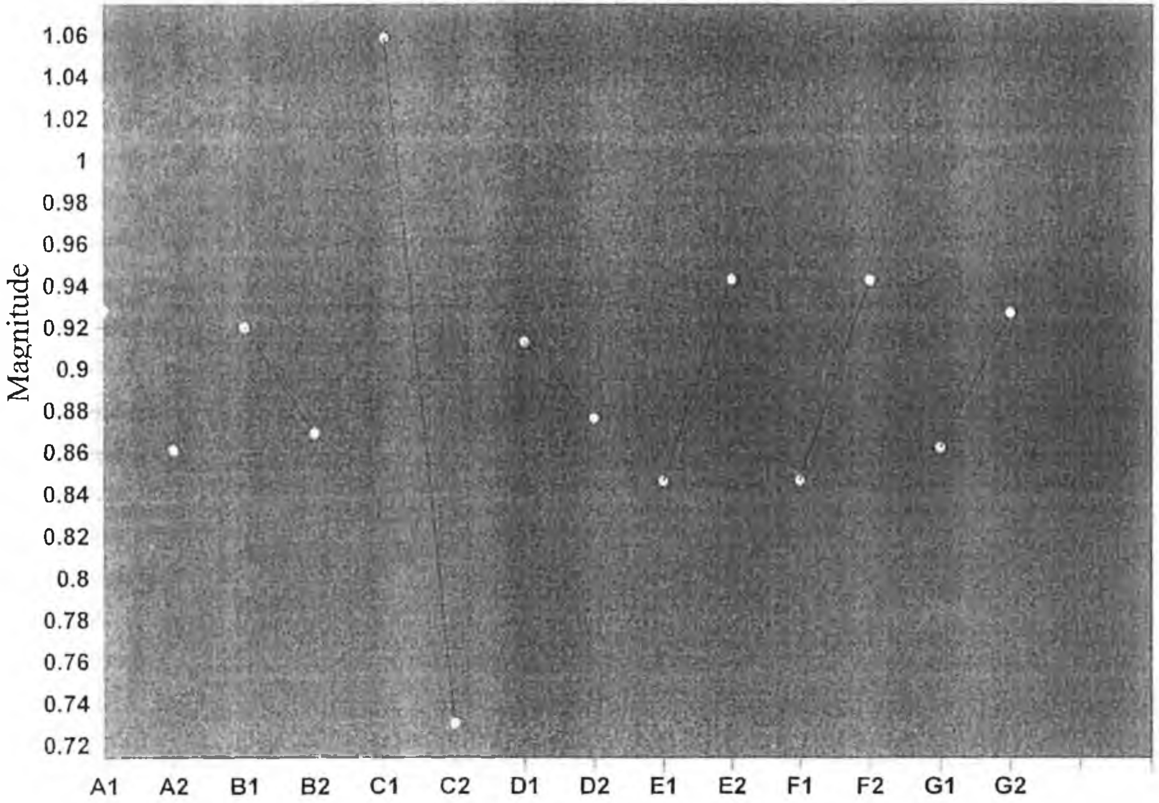
Table 6.5 Input data for c_p

Responses

File: DOE15MM.ANV Friday, April 18, 2003, 10:04:14

Experiment: 15 mm OC Data: DOE Analysis
More: More:

Mean Analysis



Signal/Noise Analysis

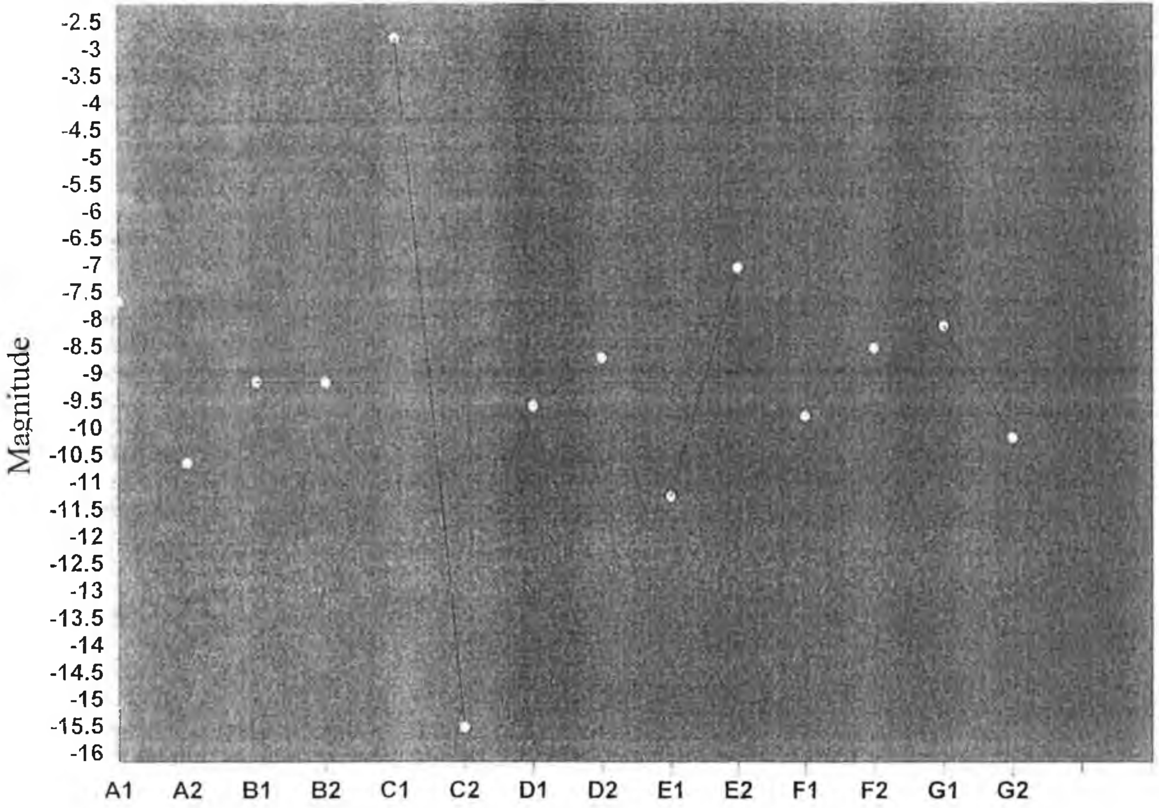


Table 6.6 Response signal for Mean analysis and Signal/noise for c_p

Experimental Layout

File: DOE15MMW.ANV　Friday, April 18, 2003, 10:00:13

Experiment: 15 mm OC
More:

Data: DOE Analysis
More:

Labels for Group 1

	Label	Factor Name	Level 1	Level 2
1	A	Temperature (°C)	25	35
2	B	Time (seconds)	180	200
3	C	Voltage (Volts)	3	3.5
4	D			
5	E	Acid Content (Molar)	3	4
6	F	Metal Content (grams/liter)	0	2
7	G			

Group 1 OA

	A	B	C	D	E	F	G
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

Experimental data
Data type is Non-Classified
Signal-to-Noise ratio is Smaller the Better

Group 1	Rep.	1	2	3
1		25.6800	21.7700	21.8500
2		22.9500	14.5400	19.5500
3		28.5000	32.5900	27.6700
4		22.5000	14.3000	24.8300
5		29.2500	31.4900	19.9800
6		48.5600	38.9200	42.9800
7		26.9900	29.5800	29.4300
8		32.7100	29.4300	32.7100

Table 6.7 Input data for mass removal

Responses

File: DOE15MMW.ANV Friday, April 18, 2003, 10:03:33

Experiment: 15 mm OC Data: DOE Analysis
More: More:

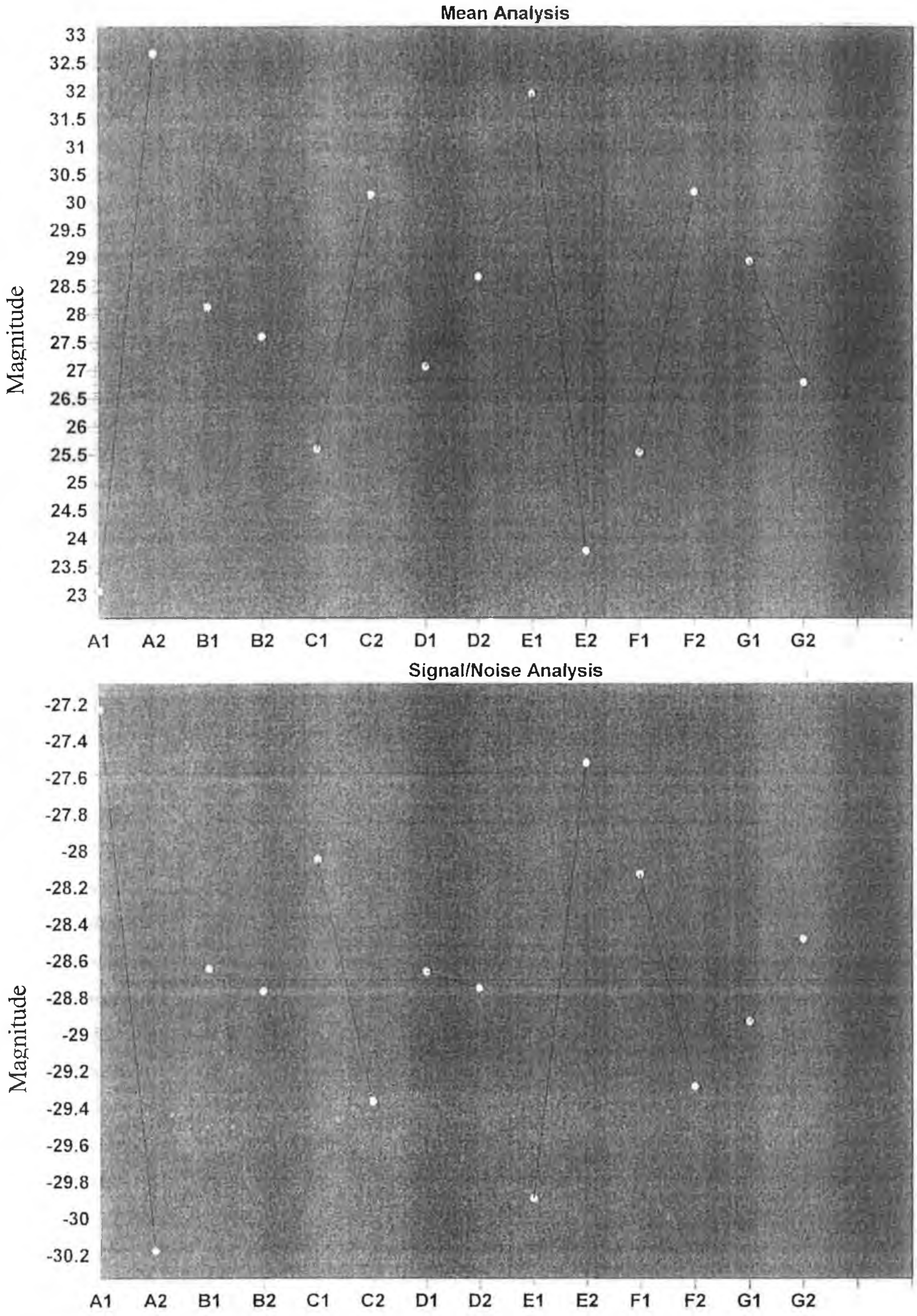


Table 6.8 Response signal for Mean analysis and Signal/noise for mass removal

6.4 Processing of Results

The values of the Smartscope measurements (Cp) and visual inspection (rating 0.0-1.0) were entered into the ANOVA software and from this the optimum settings for the experiments were determined.

The experimental layout for this DOE can be seen in Table 6.5 and respectively 6.7 for mass removal.

The optimum settings for the experiments can be seen in the response graphs (Table 6.6 and table 6.8 for Cp and visually inspection respectively table 6.9 and 6.10 for mass removal).

From this it can be determined that the optimum settings for a given stent design are:

Factor	Setting
Temperature (°C)	25
Time (seconds)	180
Voltage (Volts)	3
Acid Content (Molar)	4
Iron Content (grams/liter)	2

Table 6.9 Optimum Settings for the 15 mm GMIT stent using electro-etching method of cleaning

6.5 Verification of Results

A verification run was performed with 15mm GMIT stents and it was found that a clean surface visually and an excellent C_P value was achieved. It has been confirmed that the experiment was successful and that these parameters are the ones for electro-etching. Results of this experiment can be seen in Tables 6.10 and 6.11.

	Pitting	**Burnt Struts**	**Excessive Metal Removal**	**Comment**	**Rating***
Verification Experiment	No	No	No	Very clean. Excellent result.	1.0

- Rating 0.0-1.0 (1.0 being best)

Table 6.10 Visual Inspection of Verification Experiment

Process Capability (CP)	
Verification Experiment	
Symmetrical S	1.93
Flat	1.54
Arrow	1.74
Overall Average	1.736

Table 6.11 C_P of Verification Experiment

Chapter 7

Conclusions and Recommendations

7.1. Conclusions

Electrochemical surface treatment, namely electro-etching was found to have no effect on surface texture of 316L stent. It was found that electro-etching has identically effects in comparison with Chemical Etching.

Duration of ultrasonic waves was considerable decreased by using electro-etching. This means that overall time process of stent manufacturing is decreased. A comparison between metal removal in both processes shows that there is no significant difference.

An important part of the thesis was focused in controlling the process of dissolution by using different parameters and their interaction in a defined range.

The electro-etched stent has passed after visual inspection and also dimensional inspection. It has been prove that there is no difference in surface quality between these descaling processes. First conclusion is that chemical etching is a step that can be easily replaced by electro-etching.

Analyses using Scanning Electron Microscopy and Atomic Force Microscopy were employed to prove that new processes such as electro-etching could be easily replace processes that are longer and can damage the struts of the stent. There was very little, if any, differences found in the optical appearance and roughness values between stents with the optimum electro-etching conditions found by an industry standard electrochemical finish.

7.2. Recommendations

1. Fatigue testing should be carried out on the stent devices with the different parameters to establish any differences in life-time of an electro-etched stent comparing with chemical etched stent results.

2. Corrosion testing should be carried out on the stent devices cleaned with different electro-etching parameters to establish any differences in pitting potential.

3. Further SEM examinations should be carried out on failed 316L and L605 fatigue and corrosion fatigue specimens, to establish any mechanisms of failure.

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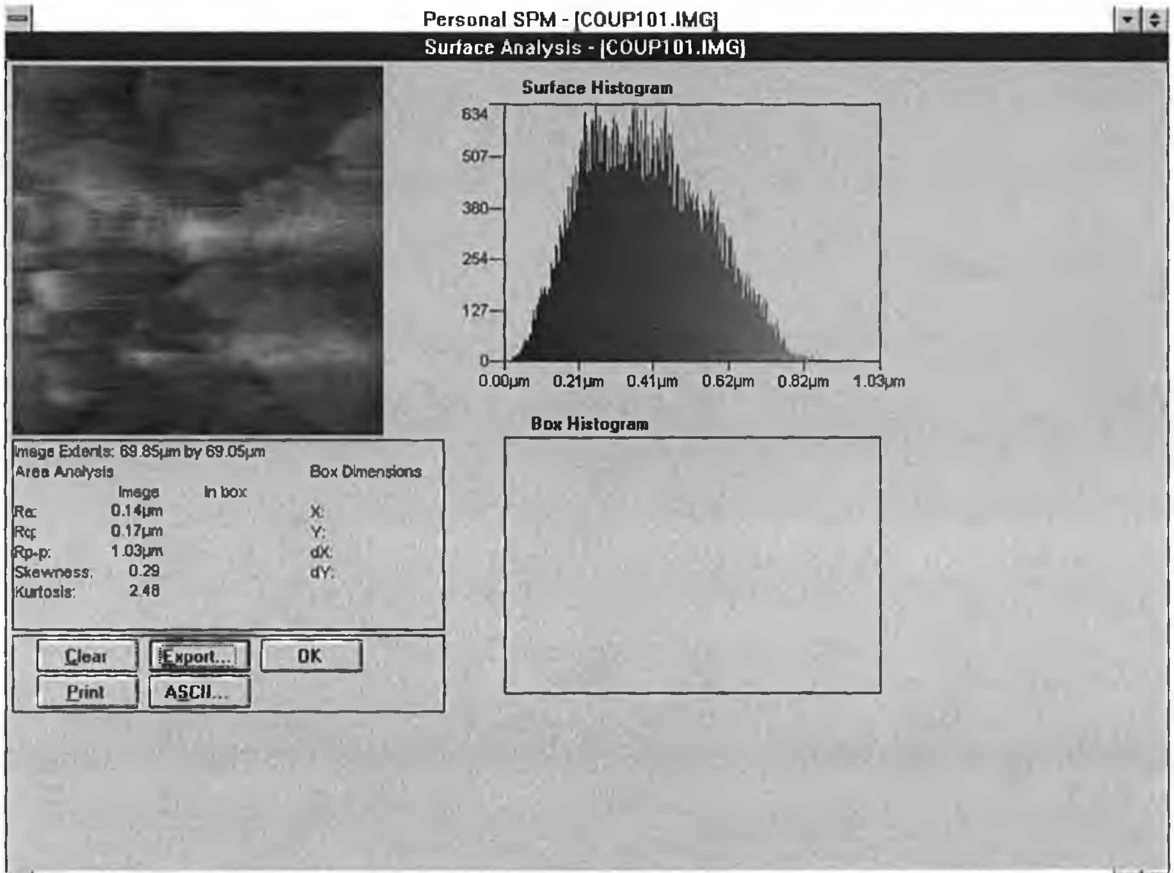


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.14µm		X:
Rq:	0.17µm		Y:
Rp-p:	1.03µm		dX:
Skewness:	0.29		dY:
Kurtosis:	2.48		

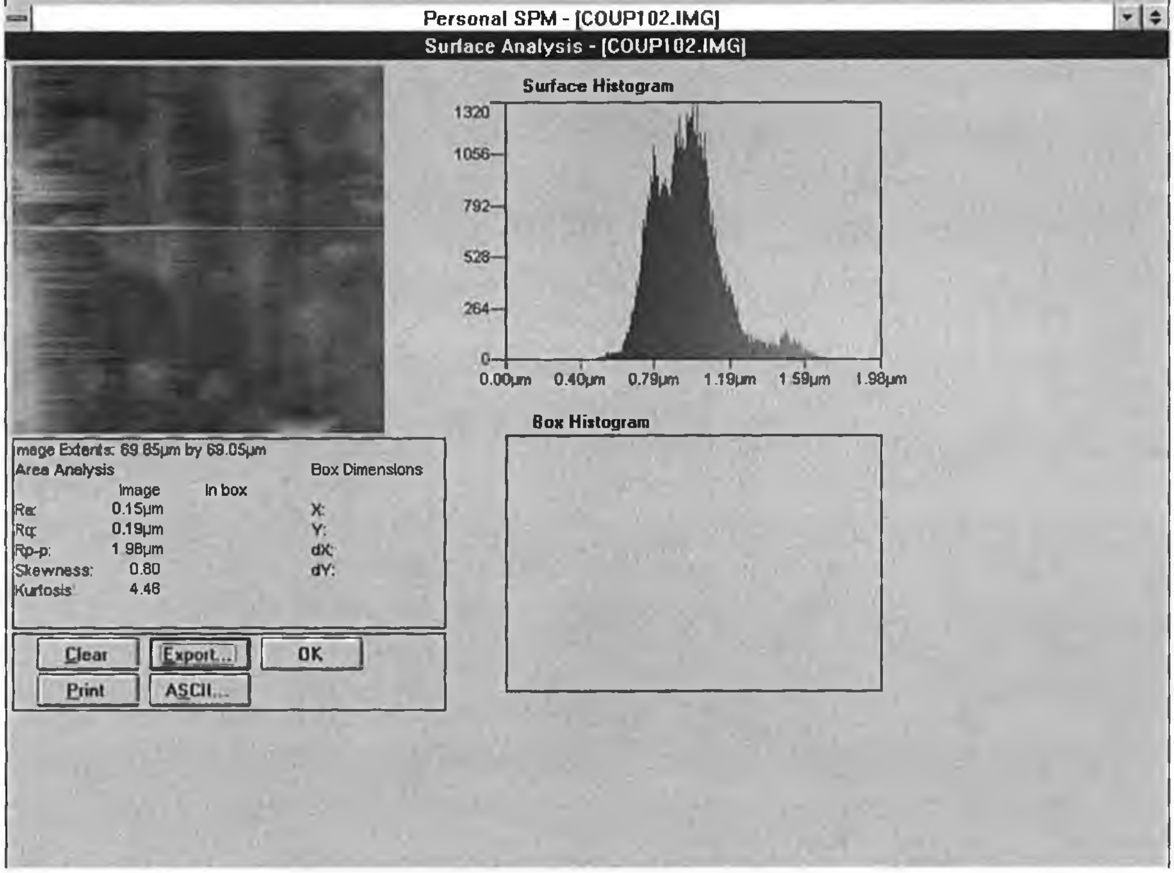


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.15µm		X:
Rq:	0.19µm		Y:
Rp-p:	1.98µm		dX:
Skewness:	0.80		dY:
Kurtosis:	4.46		

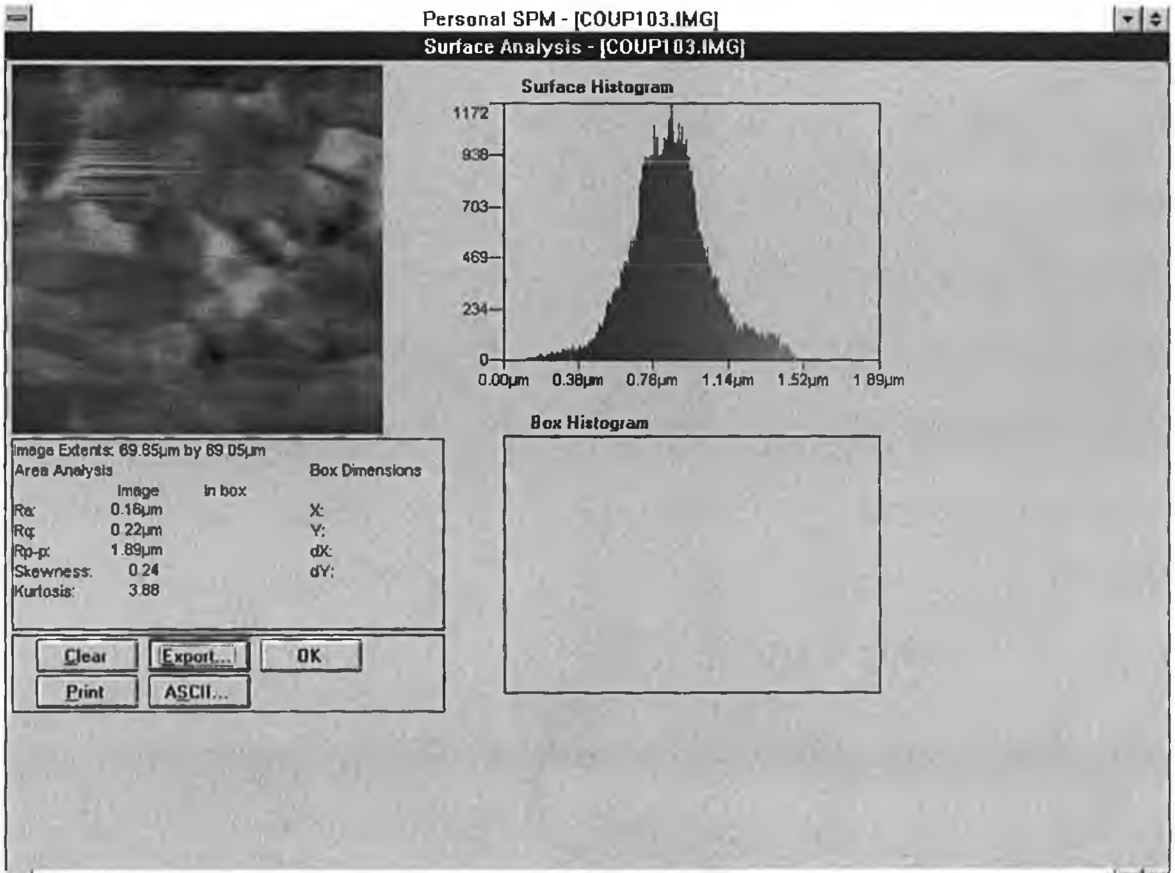


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.16µm		X:
Rq:	0.22µm		Y:
Rp-p:	1.89µm		dX:
Skewness:	0.24		dY:
Kurtosis:	3.88		

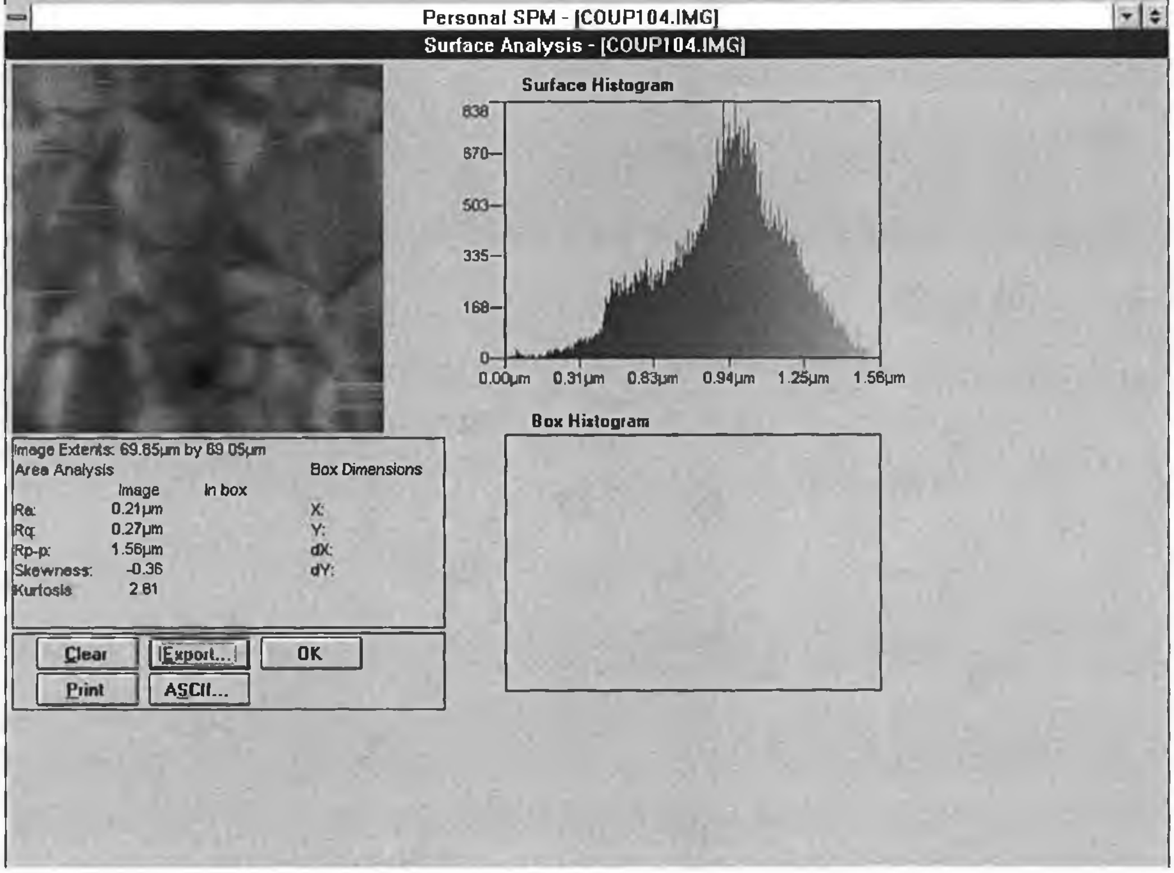


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.21µm		X:
Rq:	0.27µm		Y:
Rp-p:	1.56µm		dX:
Skewness:	-0.36		dY:
Kurtosis	2.61		

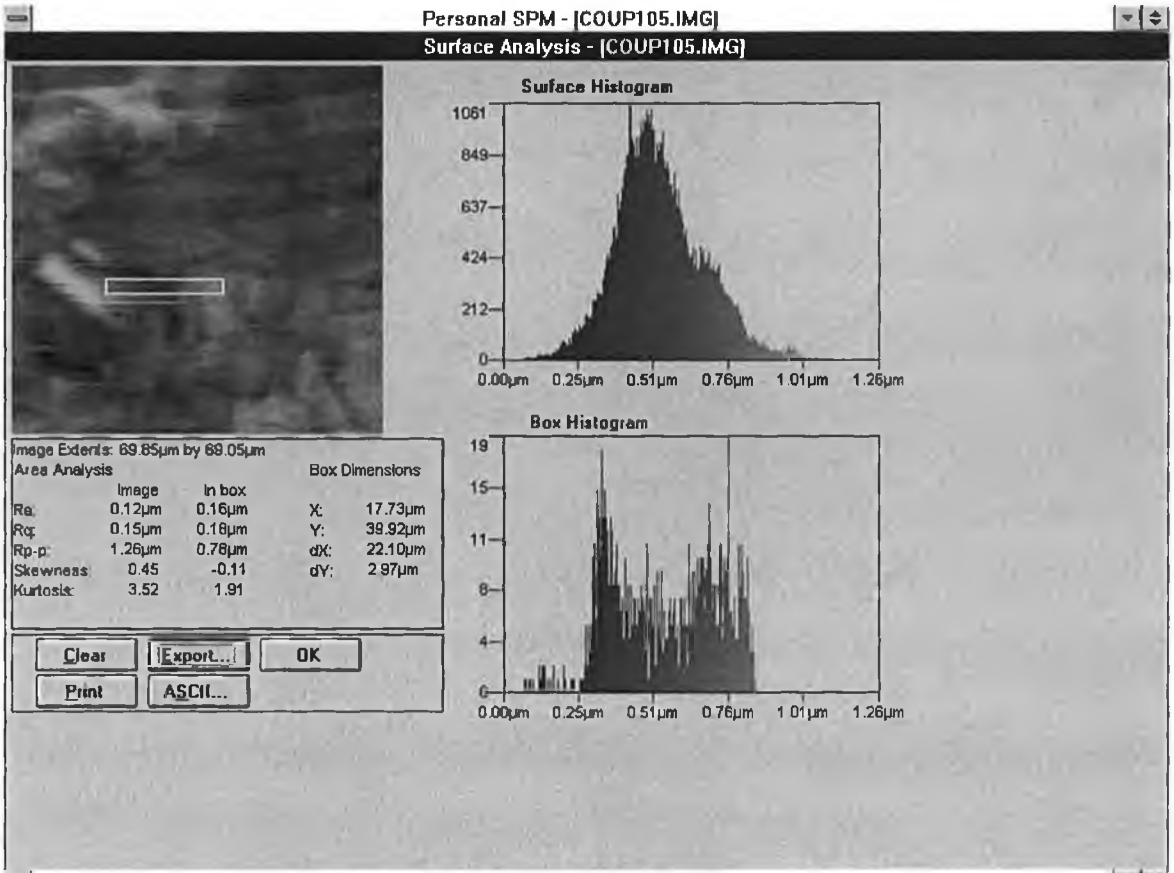


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions	
Ra:	0.12µm	0.16µm	X:	17.73µm
Rq:	0.15µm	0.18µm	Y:	39.92µm
Rp-p:	1.26µm	0.78µm	dX:	22.10µm
Skewness:	0.45	-0.11	dY:	2.97µm
Kurtosis:	3.52	1.91		

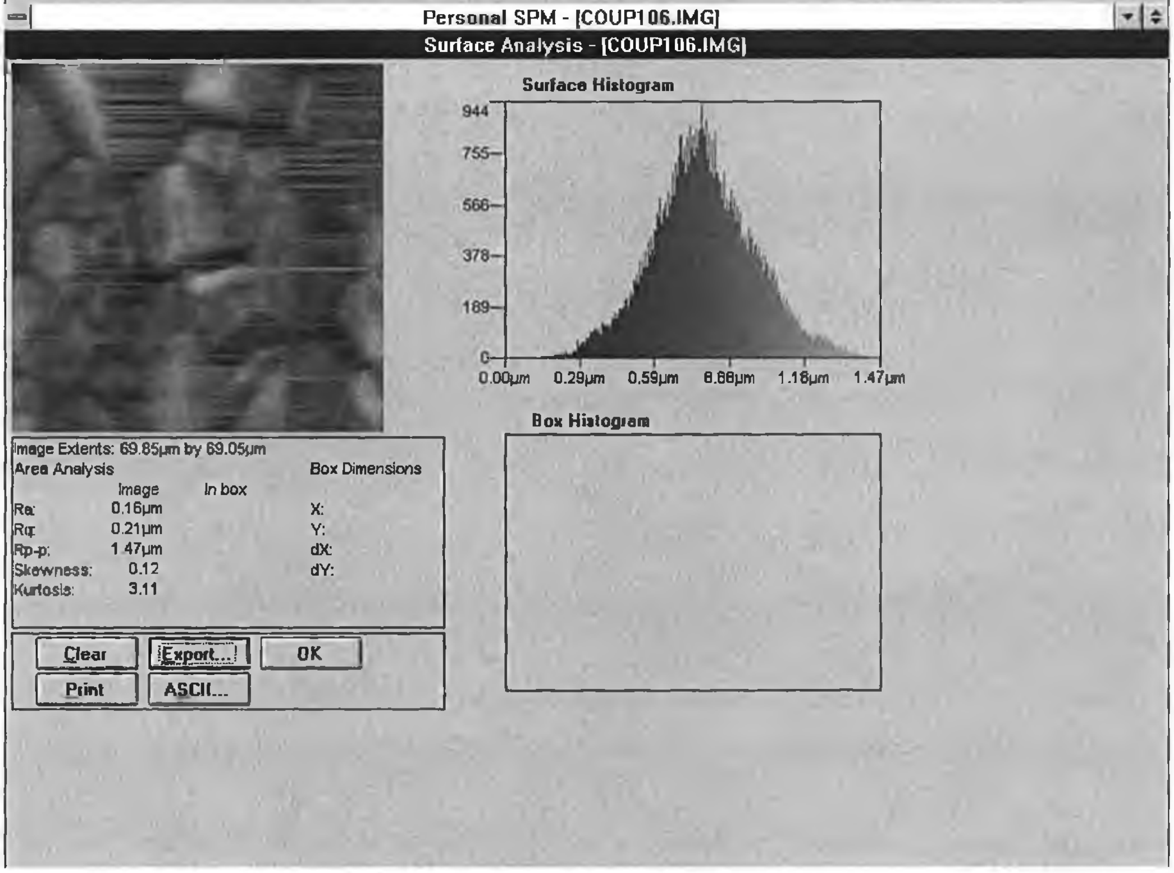


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions	
Ra:	0.16µm		X:	
Rq:	0.21µm		Y:	
Rp-p:	1.47µm		dX:	
Skewness:	0.12		dY:	
Kurtosis:	3.11			

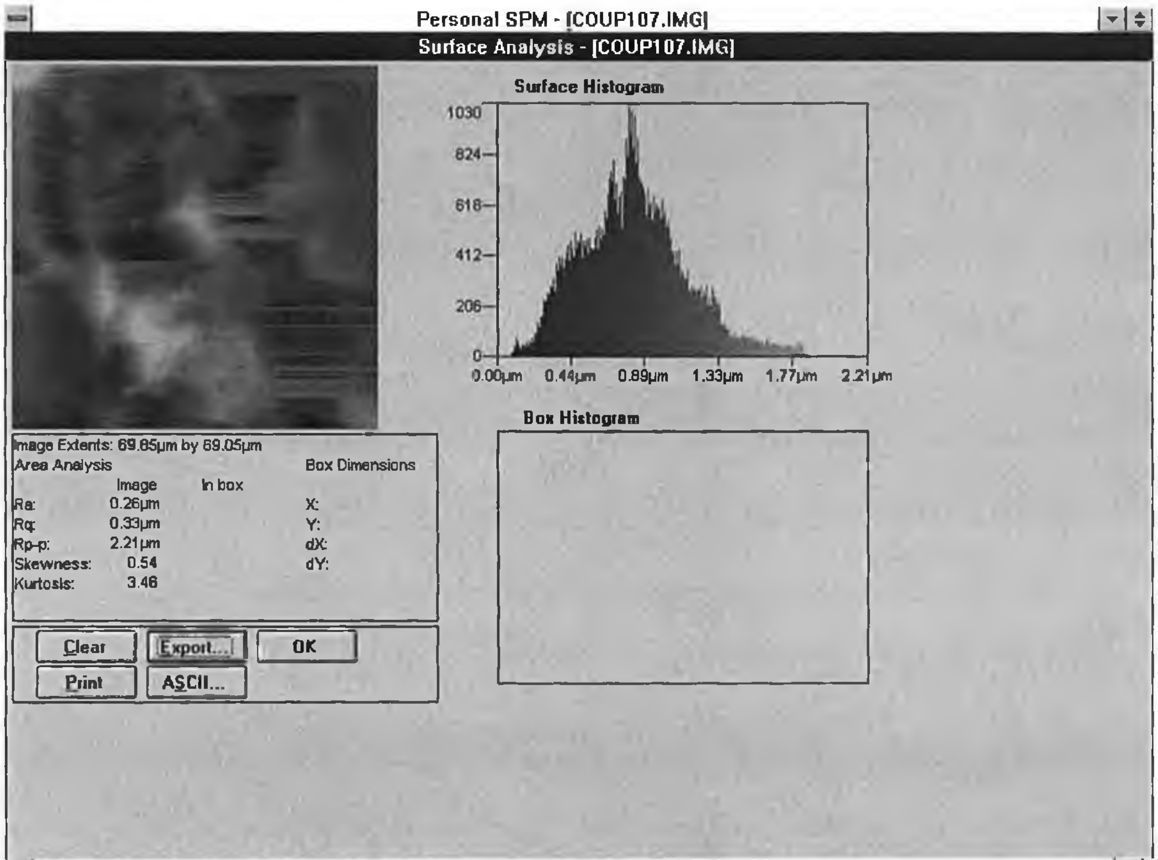


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box
Ra:	0.26µm	
Rq:	0.33µm	
Rp-p:	2.21µm	
Skewness:	0.54	
Kurtosis:	3.46	

Box Dimensions

X:

Y:

dX:

dY:

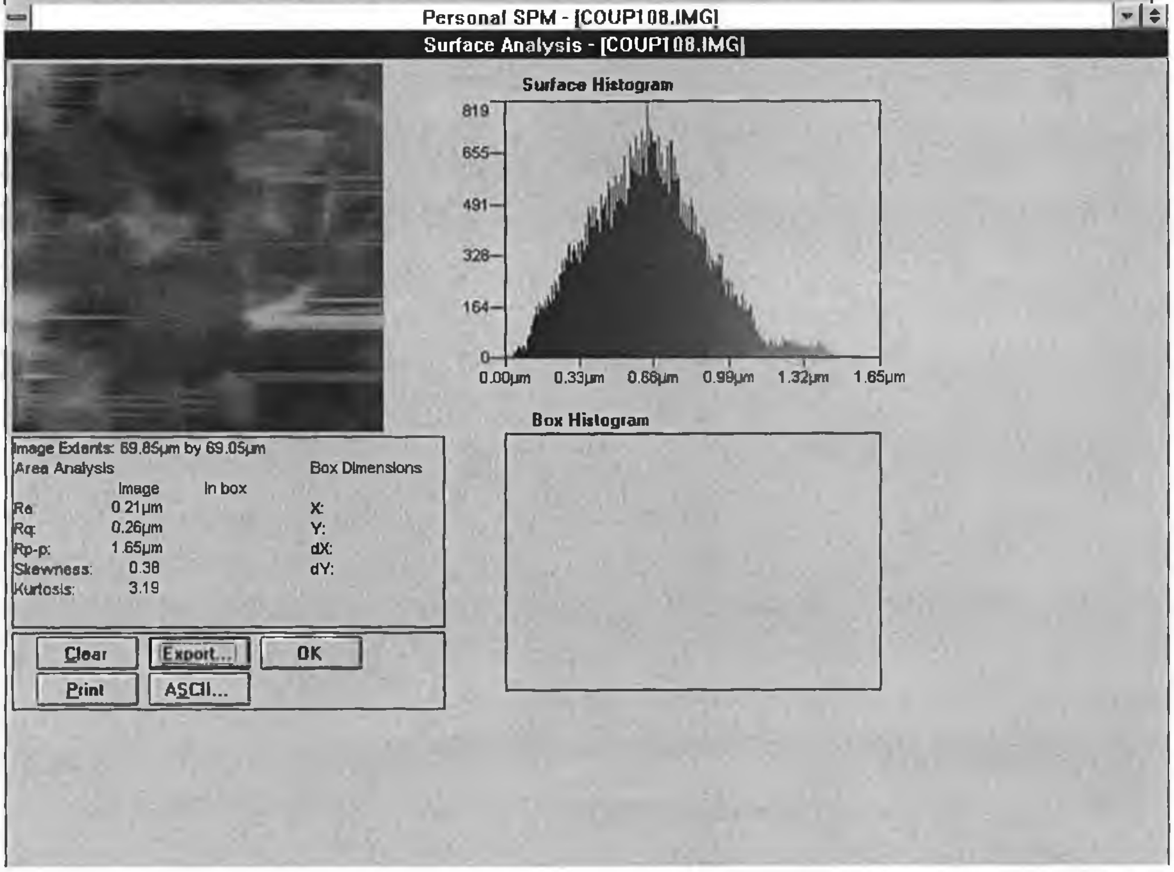


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box
Ra:	0.21µm	
Rq:	0.26µm	
Rp-p:	1.65µm	
Skewness:	0.38	
Kurtosis:	3.19	

Box Dimensions

X:

Y:

dX:

dY:

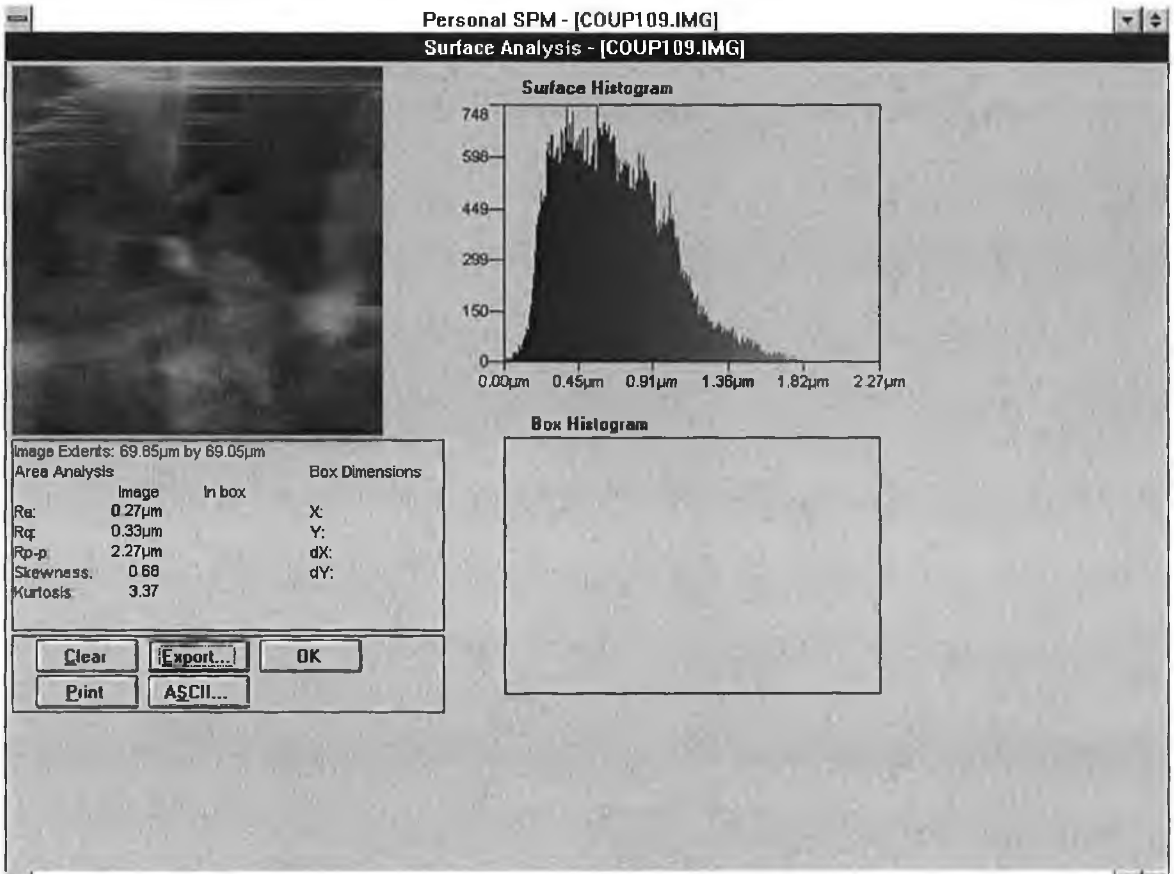


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box
Ra:	0.27µm	
Rq:	0.33µm	
Rp-p:	2.27µm	
Skewness:	0.68	
Kurtosis:	3.37	

Box Dimensions

X:
Y:
dX:
dY:

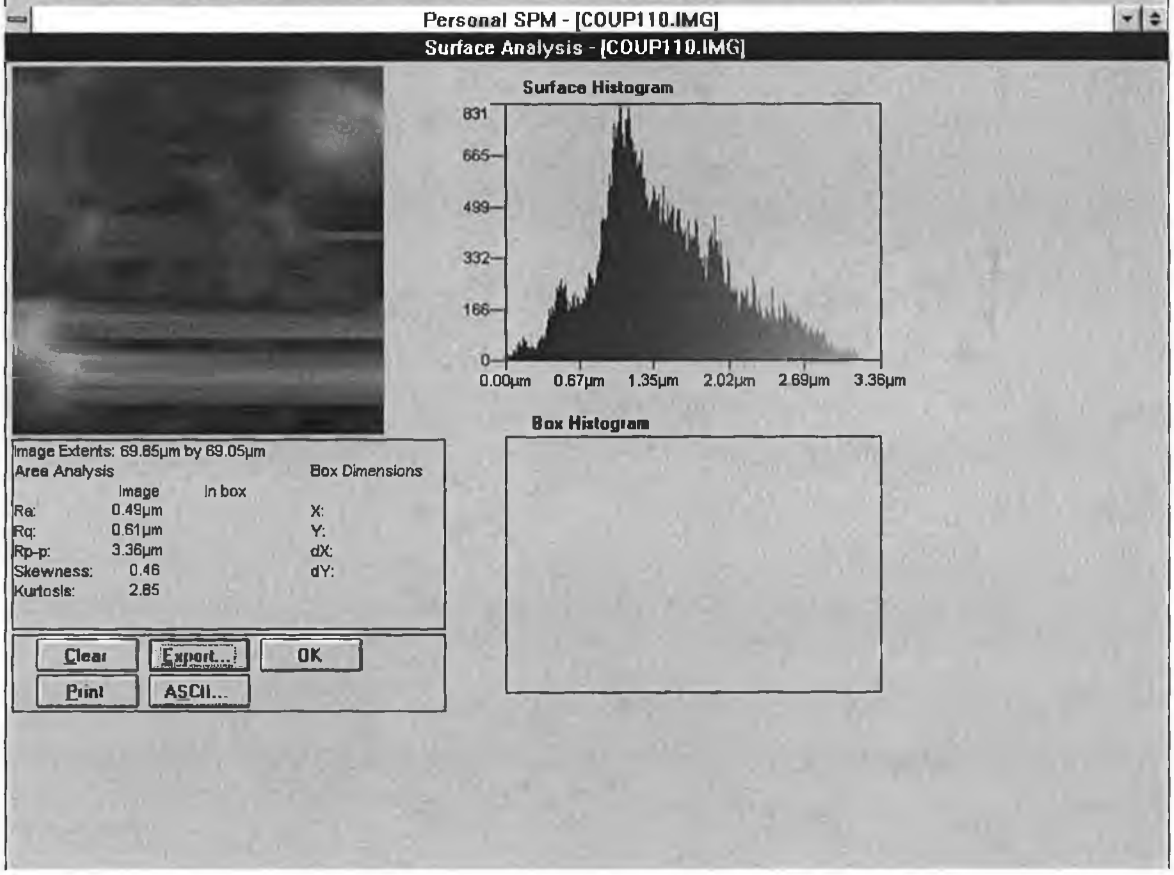


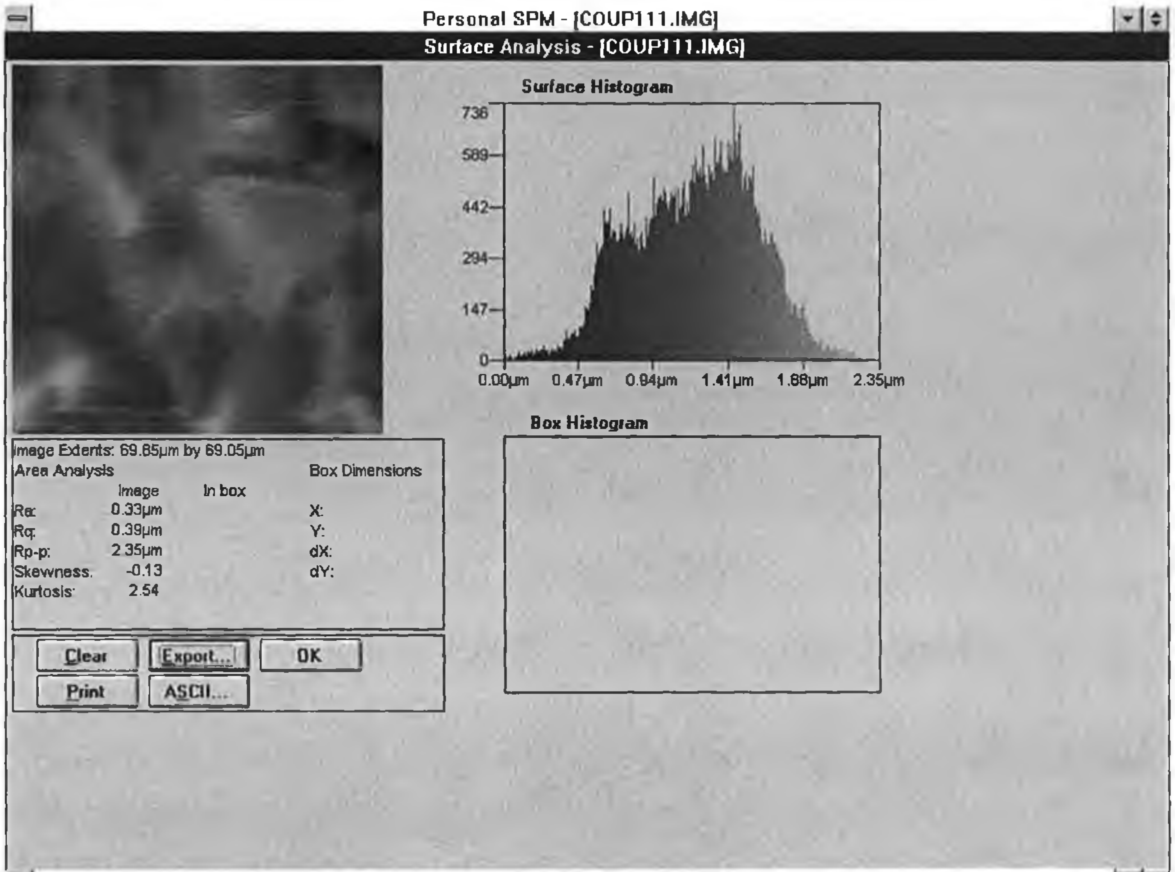
Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box
Ra:	0.49µm	
Rq:	0.61µm	
Rp-p:	3.36µm	
Skewness:	0.46	
Kurtosis:	2.85	

Box Dimensions

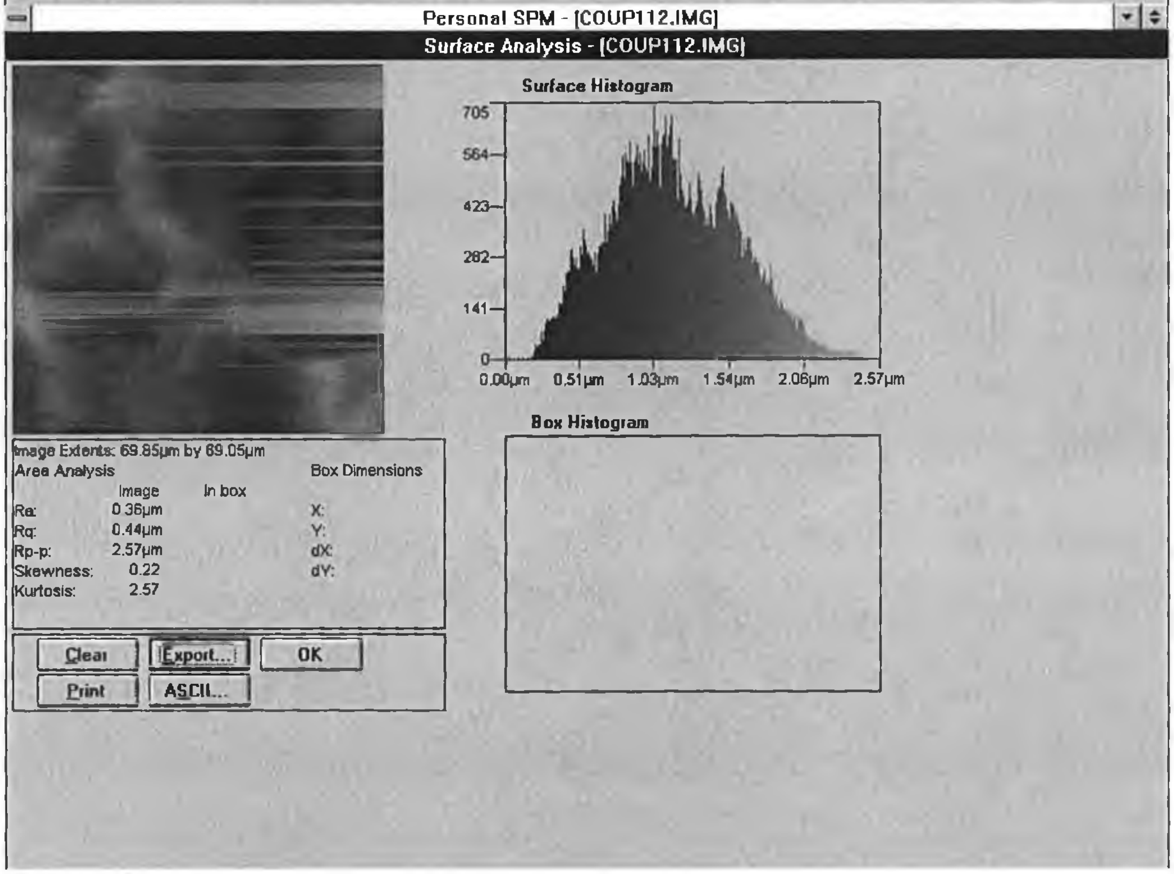
X:
Y:
dX:
dY:



Personal SPM - [COUP111.IMG]

Surface Analysis - [COUP111.IMG]

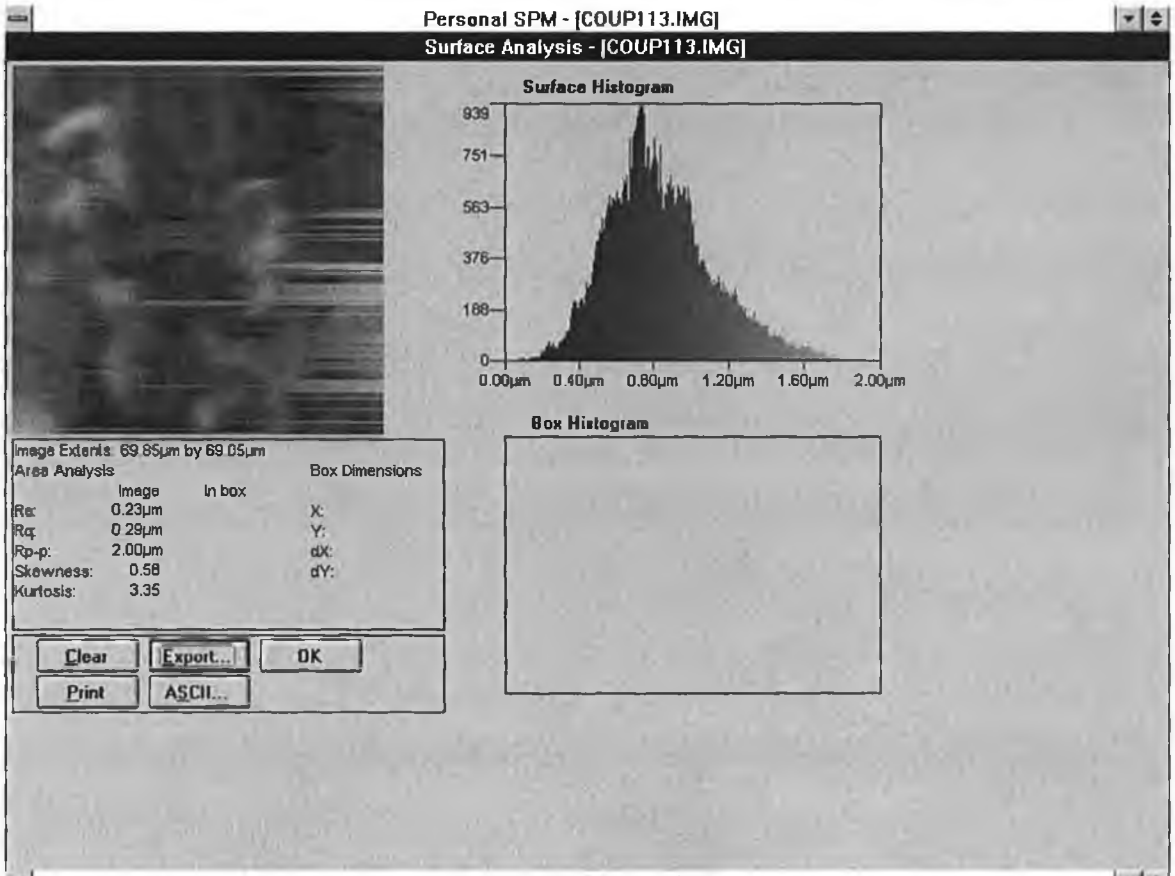
```
Image Extents: 69.85µm by 69.05µm
Area Analysis                              Box Dimensions
              Image        In box
Ra:           0.33µm                       X:
Rq:           0.39µm                       Y:
Rp-p:         2.35µm                       dX:
Skewness:     -0.13                        dY:
Kurtosis:     2.54
```



Personal SPM - [COUP112.IMG]

Surface Analysis - [COUP112.IMG]

```
Image Extents: 69.85µm by 69.05µm
Area Analysis                              Box Dimensions
              Image        In box
Ra:           0.36µm                       X:
Rq:           0.44µm                       Y:
Rp-p:         2.57µm                       dX:
Skewness:     0.22                         dY:
Kurtosis:     2.57
```



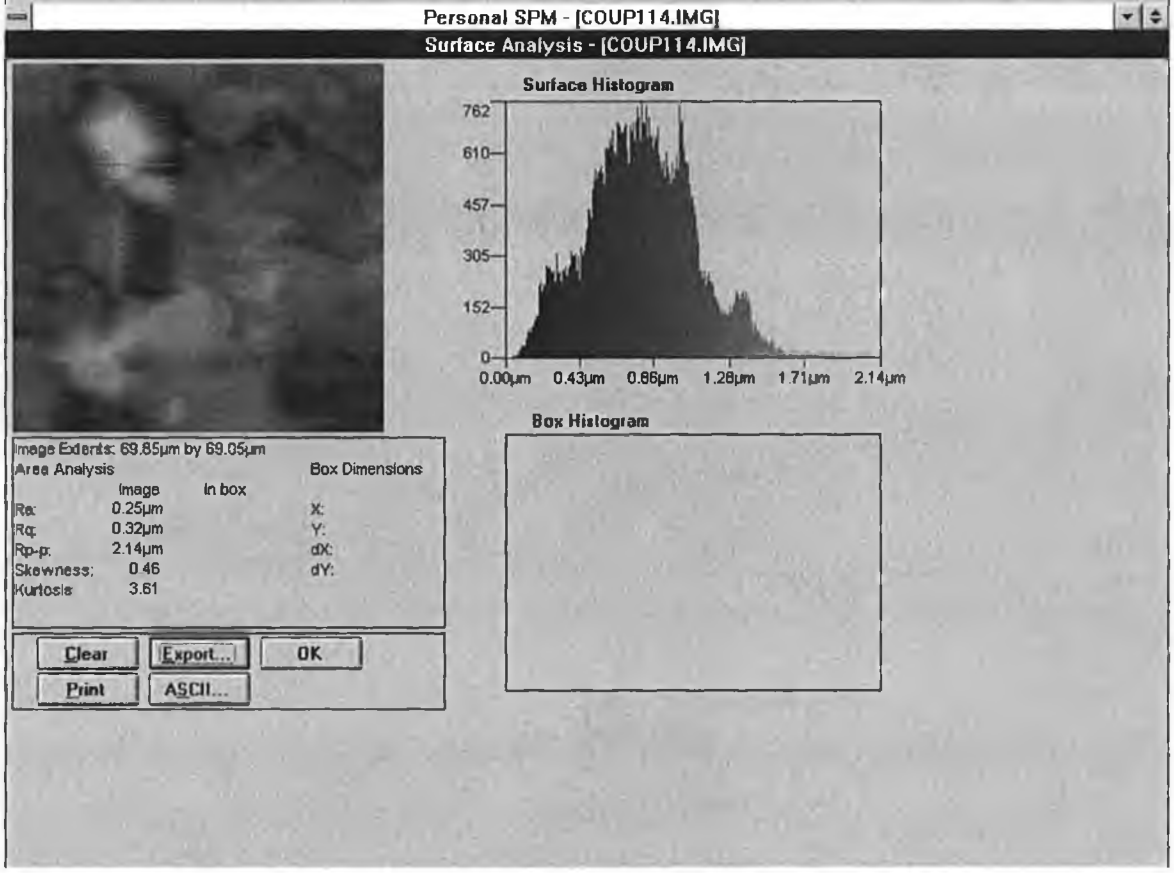
Personal SPM - [COUP113.IMG]

Surface Analysis - [COUP113.IMG]

Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.23µm		X:
Rq:	0.29µm		Y:
Rp-p:	2.00µm		dX:
Skewness:	0.58		dY:
Kurtosis:	3.35		



Personal SPM - [COUP114.IMG]

Surface Analysis - [COUP114.IMG]

Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.25µm		X:
Rq:	0.32µm		Y:
Rp-p:	2.14µm		dX:
Skewness:	0.46		dY:
Kurtosis:	3.61		

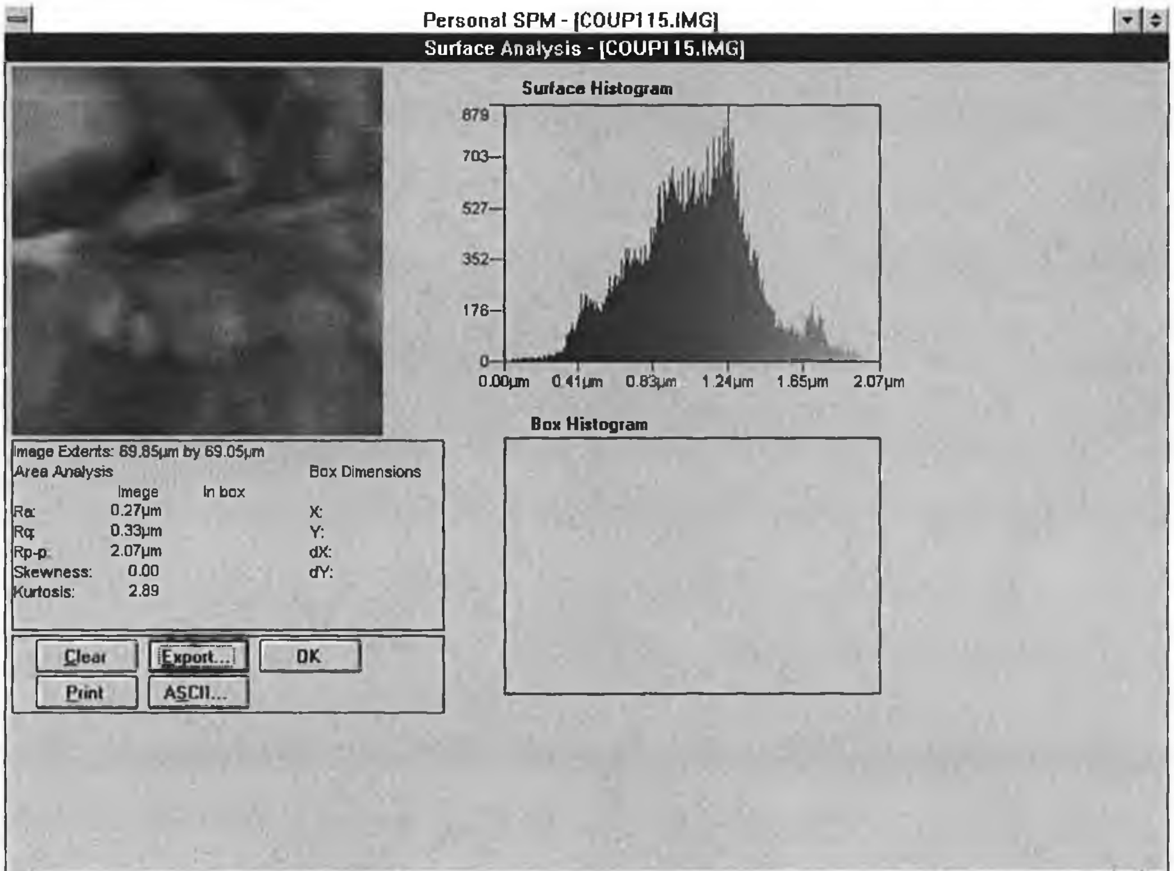


Image Extents: 69.85µm by 69.05µm
Area Analysis Image In box Box Dimensions
Ra: 0.27µm X:
Rq: 0.33µm Y:
Rp-p: 2.07µm dX:
Skewness: 0.00 dY:
Kurtosis: 2.89

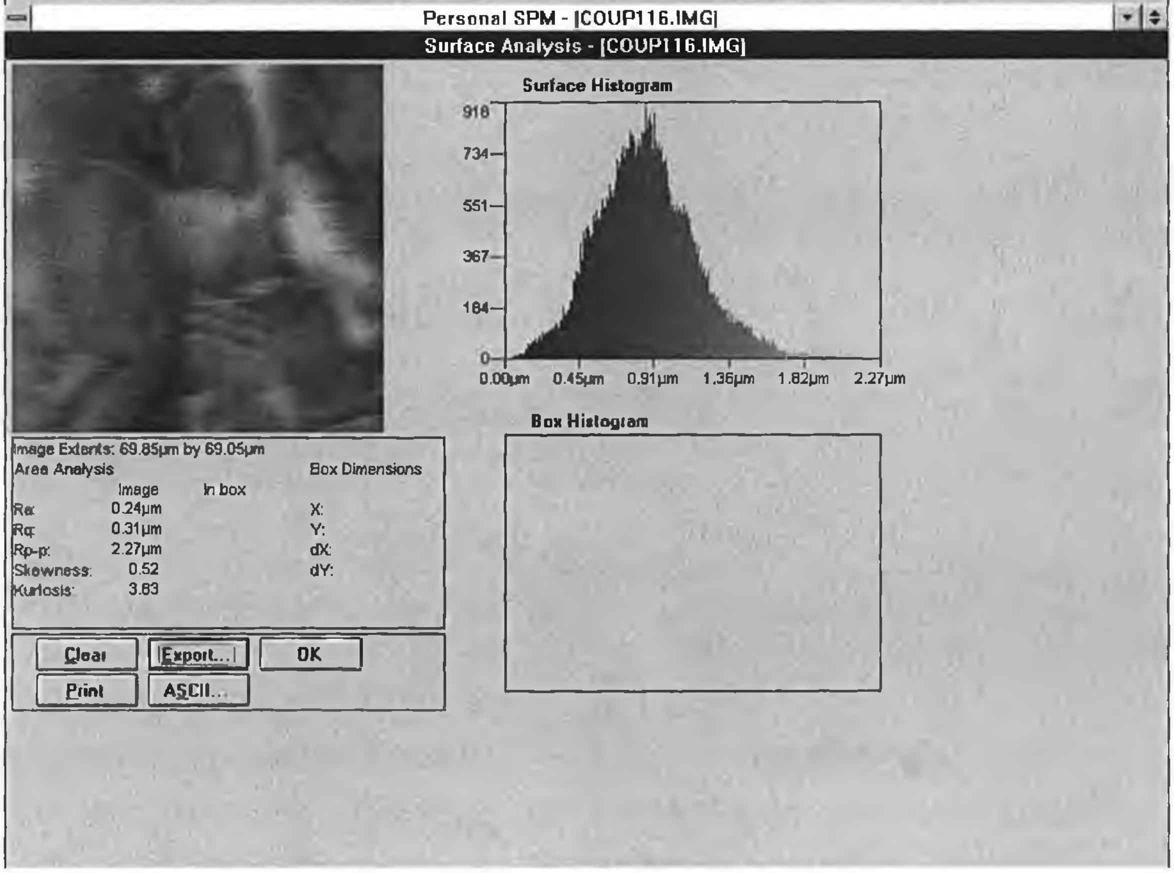
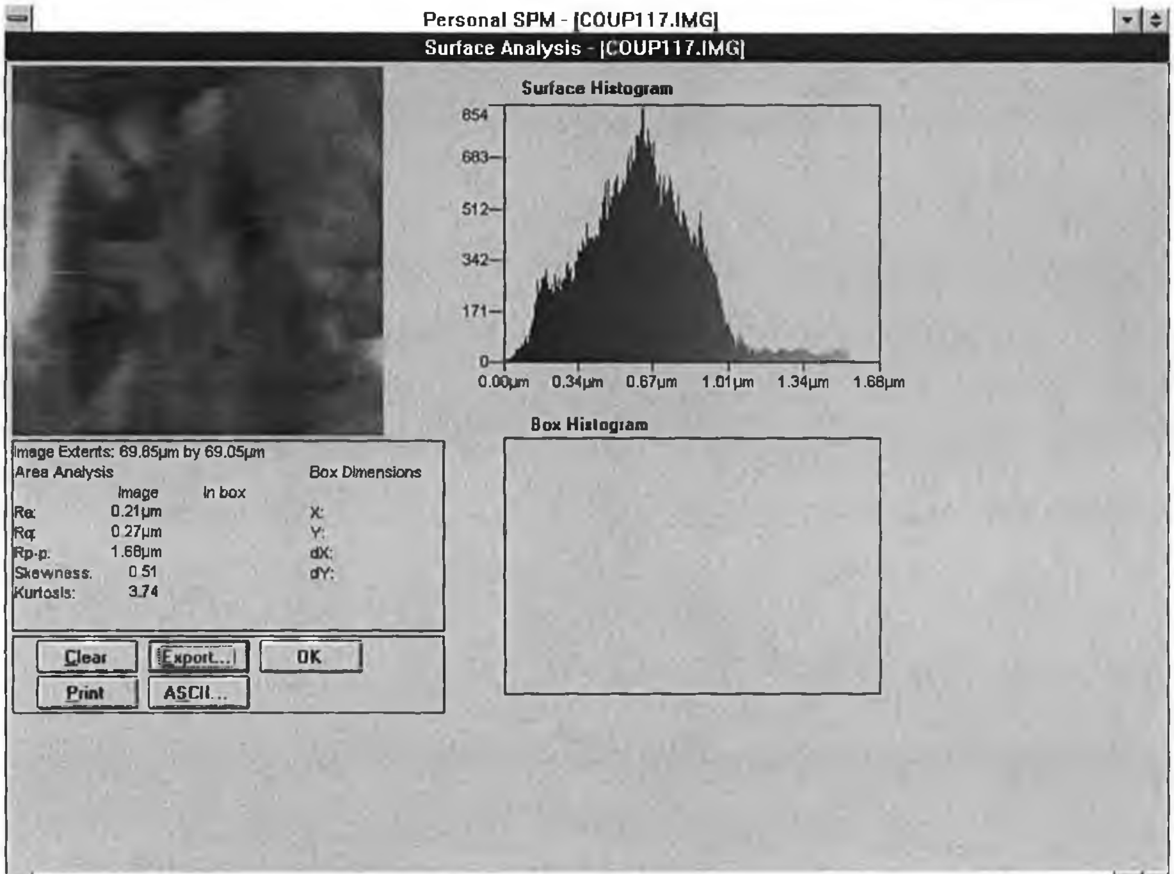


Image Extents: 69.85µm by 69.05µm
Area Analysis Image In box Box Dimensions
Ra: 0.24µm X:
Rq: 0.31µm Y:
Rp-p: 2.27µm dX:
Skewness: 0.52 dY:
Kurtosis: 3.83



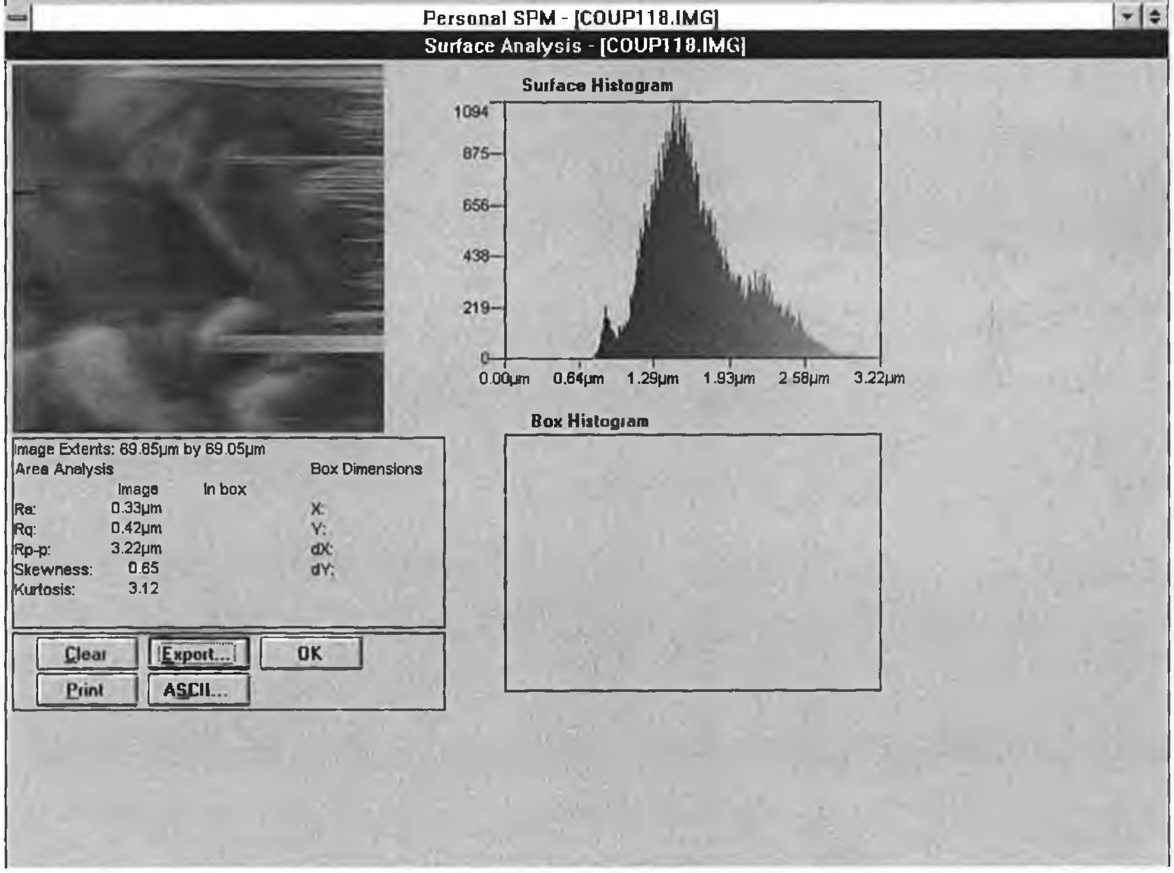
Personal SPM - [COUP117.IMG]

Surface Analysis - [COUP117.IMG]

Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.21µm		X:
Rq:	0.27µm		Y:
Rp-p:	1.68µm		dX:
Skewness:	0.51		dY:
Kurtosis:	3.74		



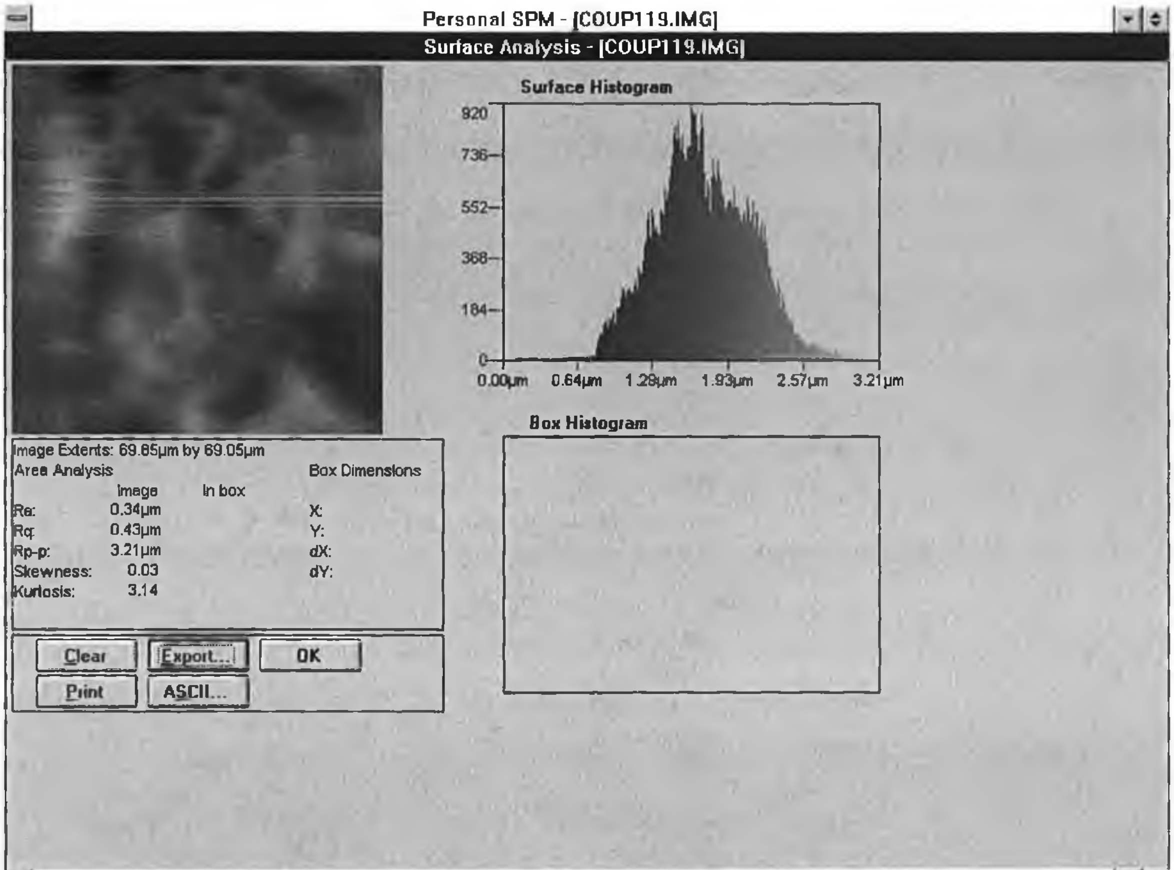
Personal SPM - [COUP118.IMG]

Surface Analysis - [COUP118.IMG]

Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.33µm		X:
Rq:	0.42µm		Y:
Rp-p:	3.22µm		dX:
Skewness:	0.65		dY:
Kurtosis:	3.12		



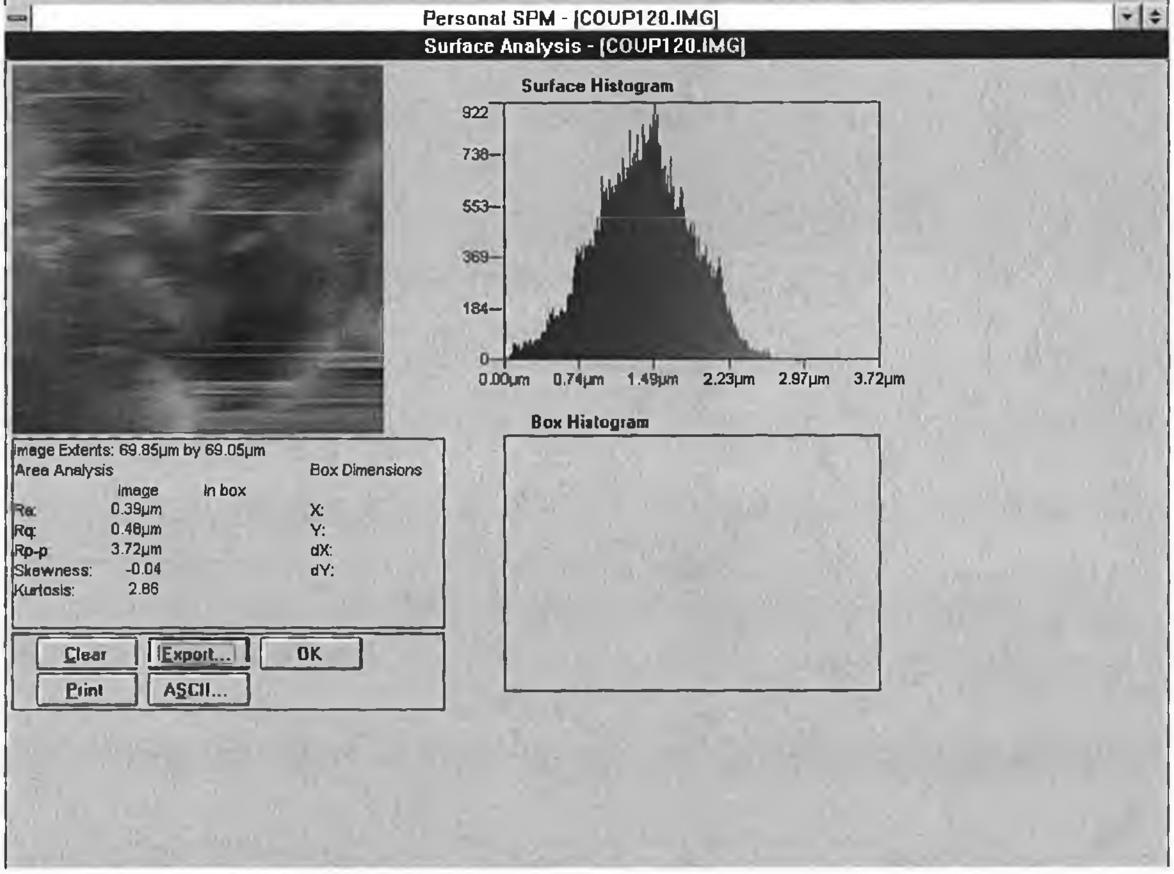
Personal SPM - [COUP119.IMG]

Surface Analysis - [COUP119.IMG]

Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.34µm		X:
Rq:	0.43µm		Y:
Rp-p:	3.21µm		dX:
Skewness:	0.03		dY:
Kurtosis:	3.14		



Personal SPM - [COUP120.IMG]

Surface Analysis - [COUP120.IMG]

Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.39µm		X:
Rq:	0.48µm		Y:
Rp-p:	3.72µm		dX:
Skewness:	-0.04		dY:
Kurtosis:	2.86		

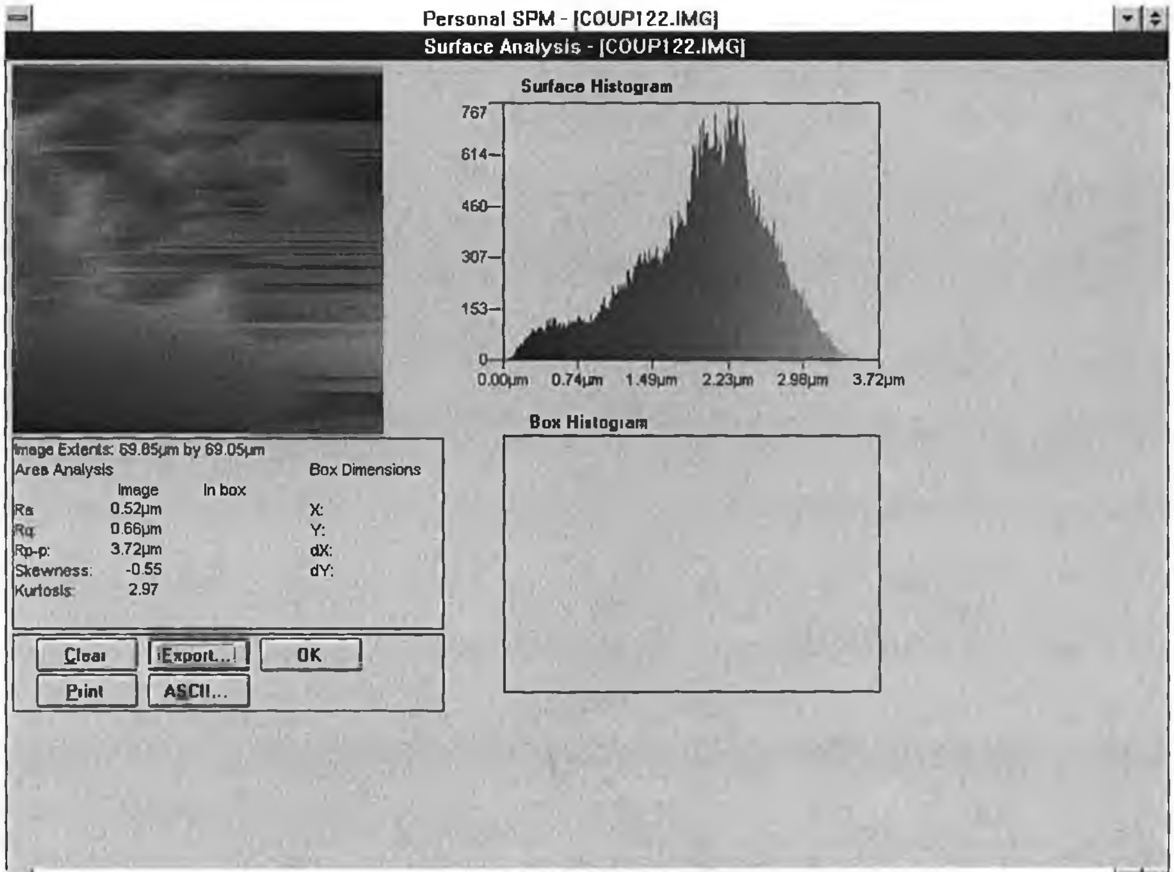


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra	0.52µm		X:
Rq	0.66µm		Y:
Rp-p:	3.72µm		dX:
Skewness:	-0.55		dY:
Kurtosis:	2.97		

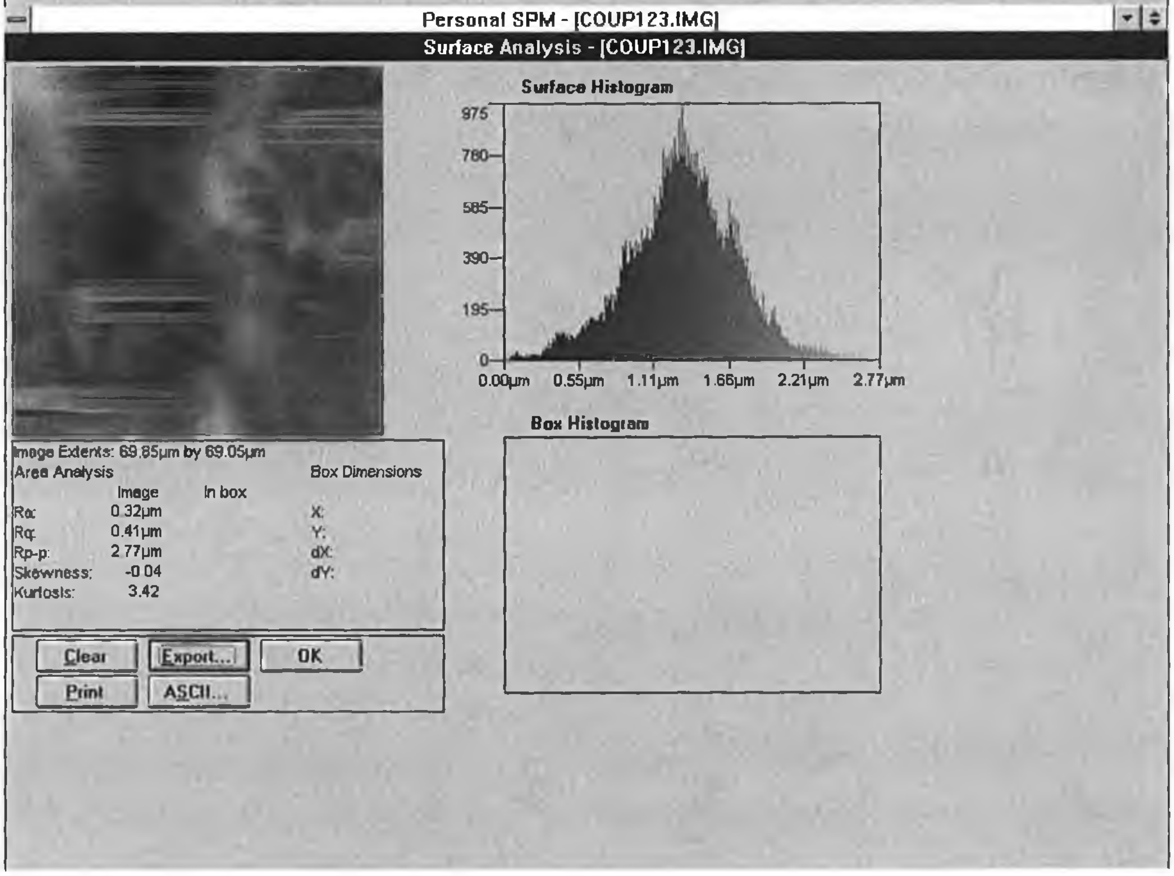


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box	Box Dimensions
Ra:	0.32µm		X:
Rq:	0.41µm		Y:
Rp-p:	2.77µm		dX:
Skewness:	-0.04		dY:
Kurtosis:	3.42		

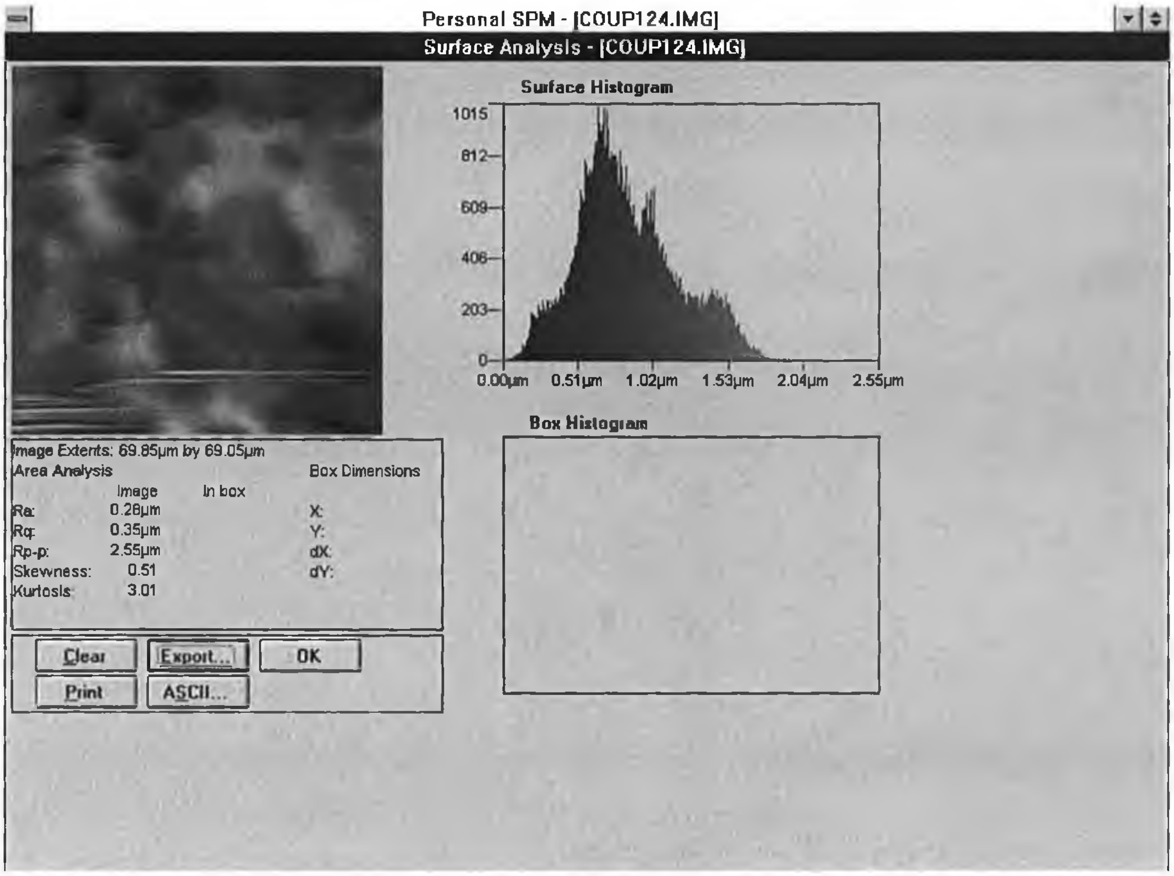


Image Extents: 69.85µm by 69.05µm

Area Analysis

	Image	In box
Ra:	0.28µm	
Rq:	0.35µm	
Rp-p:	2.55µm	
Skewness:	0.51	
Kurtosis:	3.01	

Box Dimensions

X:

Y:

dX:

dY:

The paper presented at
The 8th Annual Bioengineering in Ireland
And
The 16th Meeting of the Northern Ireland
Biomedical Engineering Society
Sligo, January, 2002

IMPROVED SURFACE QUALITY AND CORROSION RESISTANCE OF LASER CUT BIO-MEDICAL DEVICES BY THE OPTIMISATION OF SURFACE TREATMENT TECHNIQUES

1. Introduction

Several electrochemical methods are employed in the bio-medical industry because of their ability to manufacture of surface-finish metal articles, fabrications and components which are difficult or impossible to produce by traditional workshop techniques[1].

Electropolishing is a process by which metal is removed from a work piece by passage of electric current while the work is submerged in a specially-designed solution. The process is essentially the reverse of electroplating. In a plating system, metal ions are deposited from the solution onto the work piece; in an electropolishing system, the work piece itself is dissolved, adding metal ions to the solution.

The principle of differential rates of metal removal is important to the concept of deburring accomplished by electropolishing. Fine burrs become very high current density areas and are, subsequently, rapidly dissolved. Low current density areas receive lesser amounts of current and may show negligible metal removal.

2. Finishing Methods

a. Electrochemical Etching

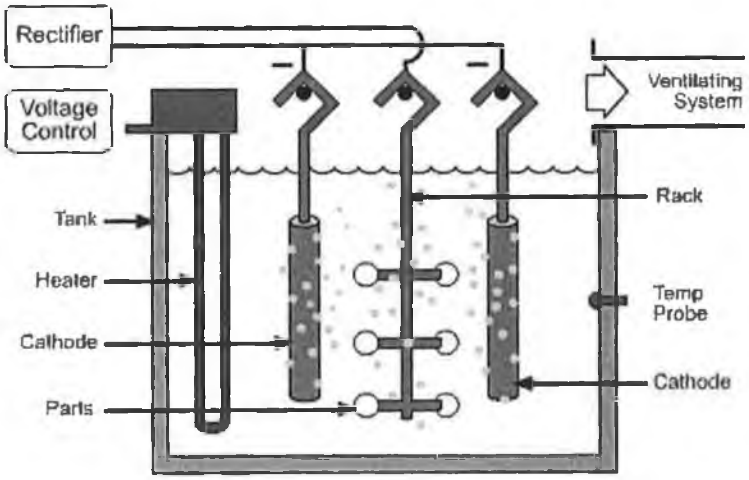


Fig. 1 Schematic Electro-etching and Electro-polishing Installation

Electrochemichal etching is the deliberate (selective) and controlled removal of an electrically conducting (or semiconducting) material in an electrolyte.

The purpose for practiseing electrochemichal etching is to control surface roughening in order to promote a better and clean surface prior to electro-polishing.

Etching of the material may be carried out either chemically under open-circuit conditions (i.e. controlled "corrosion") or it may be electrochemically driven by applying a potential. It requires no power supply or auxiliary electrodes; the electrolyte conditions are chosen such that the species to be removed is dissolved at a reasonable rate, courtesy of a simutaneous cathodic process.

Taking the case of the dissolution of a metal M, the anodic process in reaction (1) is supported by suitable electroreduction (2):

$\mathrm{M} - n\mathrm{e}^{-} \rightarrow \mathrm{M}^{n+}$ (1)

$\mathrm{X} + n\mathrm{e}^{-} \rightarrow \mathrm{X}^{n-}$ (2)

To give an overall etching process:

$\mathrm{M} + \mathrm{X} \rightarrow \mathrm{M}^{n+} + \mathrm{X}^{n-}$ (3)

Thus, the etchant must permit active dissolution of M to Mn+ while supplying a cathodic reactant X. In the general case, both Mn+ and Xn+ may affect the rate of etching, i.e. the progress of reaction (3).

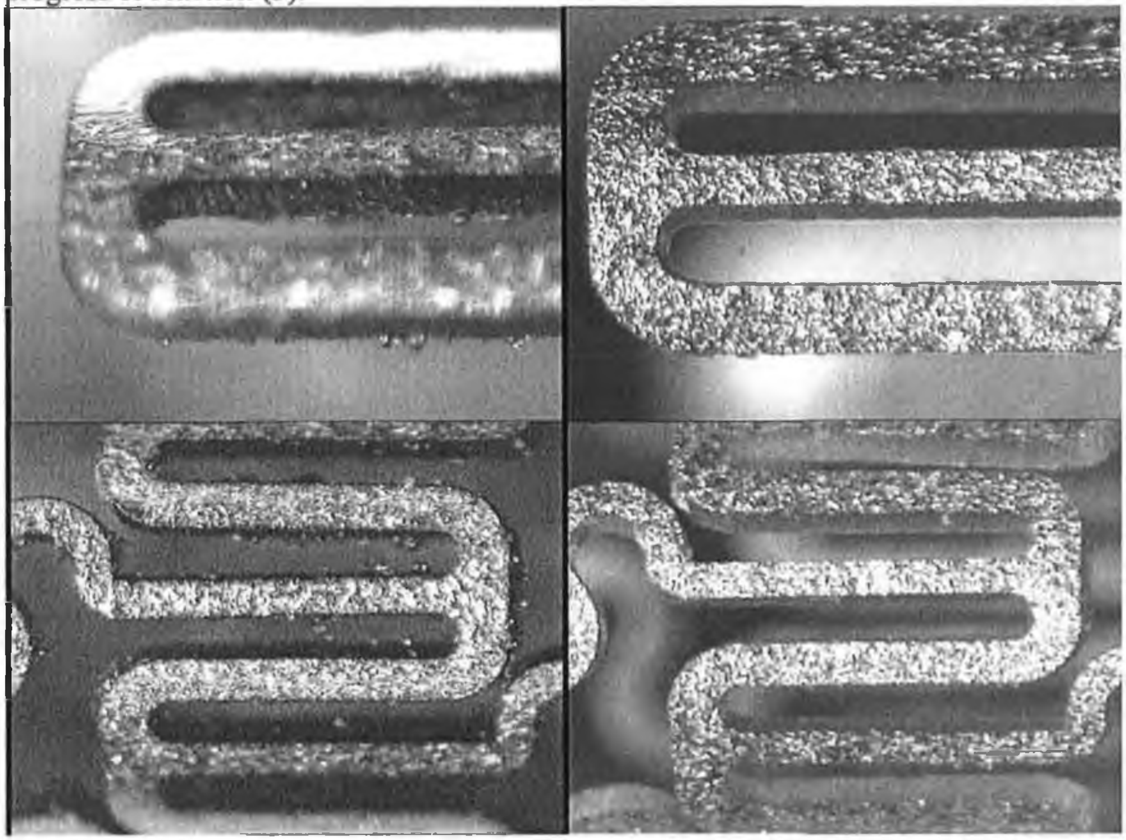


Fig. 2 –A strut of a stent before and after etching (by Microscope)

Anodic etching requires that the metal be driven to a convenient potential (positive of its open-circuit value), by means of a power supply and a suitable inert cathode such that reaction (1) proceeds at the desired rate.

The process conditions must be chosen carefully and controlled within limits to permit the etching to be sufficiently selective both chemically and physically, e.g. it may be required to etch one metal rather than another, one metallurgical phase rather than a whole matrix or an oxide rather than a metal or semiconductor.

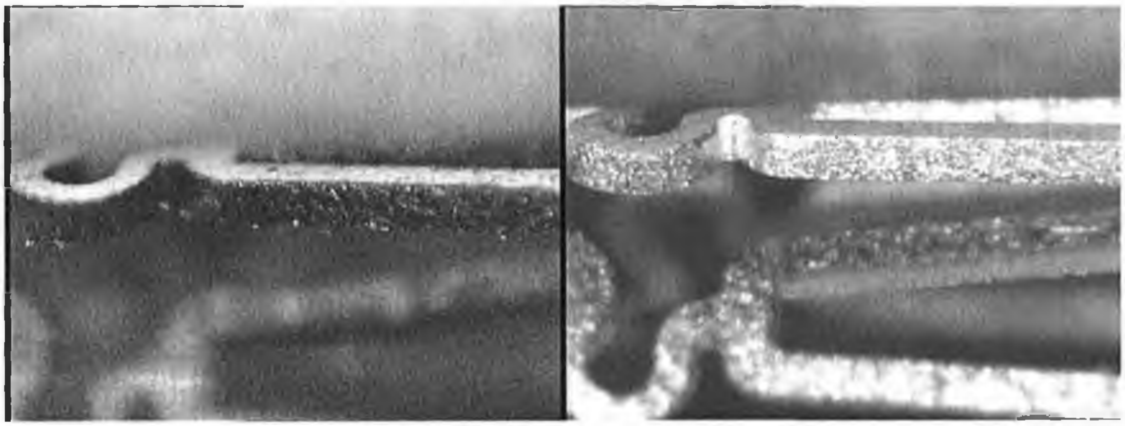


Fig. 3 Cutted surface from a stent: before and after polishing (by Microscope)

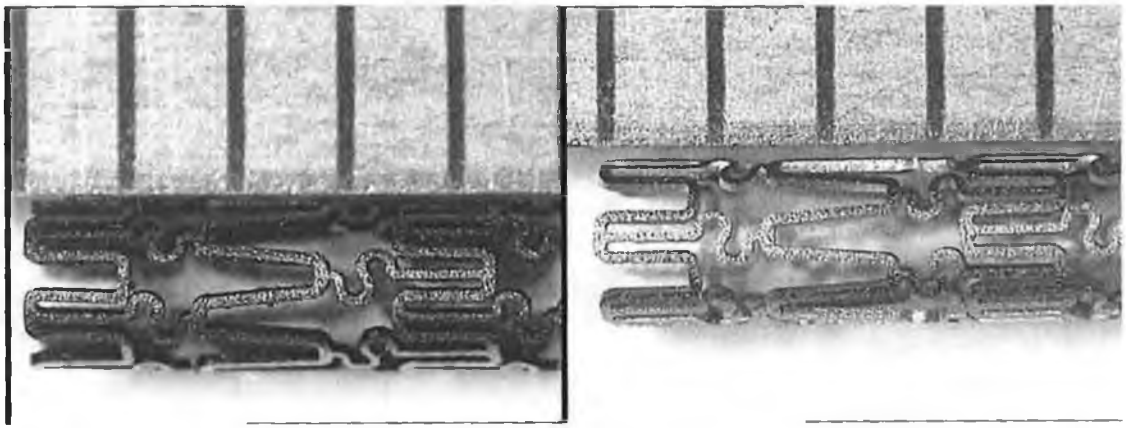


Fig. 4 A Large Vessel Stent before and after etching

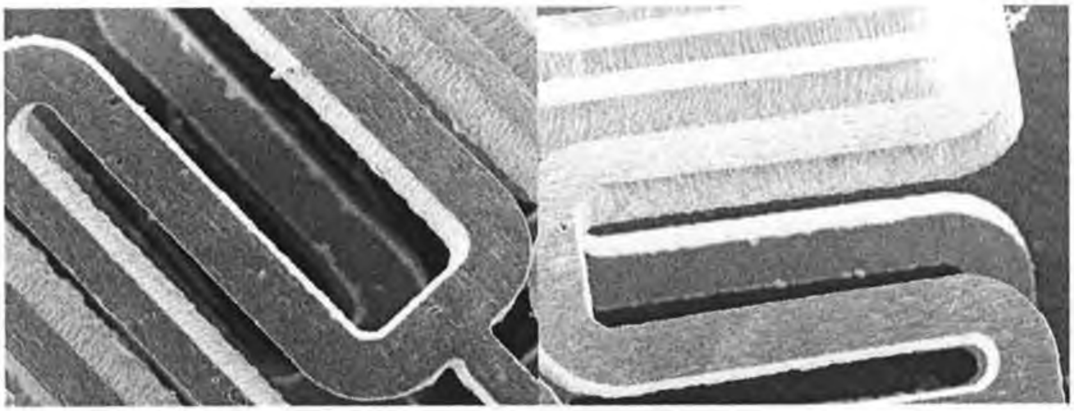


Fig. 5 Etched surfaces on a Large Vessel Stent (by SEM)

b. Electropolishing

Electropolishing is the electrolytic removal of metal in a highly ionic solution by means of an electrical potential and current. A less technical description of the process would be "reverse plating". Electropolishing is normally used to remove a very thin layer of material on the surface of a metal part or component. The process is of interest because of its ability to enhance the material properties of a work piece in addition to changing its physical dimensions.

The mechanism of electropolishing is thought to involve both selective anodic dissolution (the potenitial distribution will favour corrosion of the surface at peaks rather in troughs) and oxide film formation. Electropolishing leads to extremely reflective surfaces which, unlike mechanically polished surfaces, are stress-free. Before the process can be carried out successfully, however, the surface must already be smooth since macroroughness cannot be removed[1].

3. Factors involved in surface finish

Many of the factors which influence the rate of dissolution also affect the manner in which metal is removed from the anode, and hence they partly determine the surface finish. Of these factors, the anode potential and current density play a major part. Their role can be studied form polarisation curves.

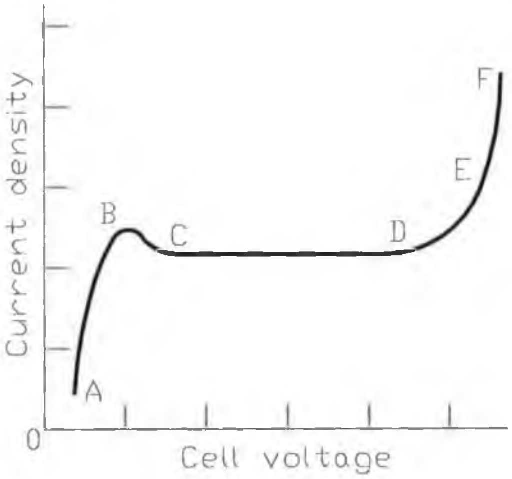


Fig.6 Ideal current density-cell voltage curve

In order to understand more about electro-polishing, plots of anode potential, cathode potential, cell voltage on current density for different process variables are generally obtained and studied. Of these, the plot of cell voltage versus current density gives more information to know the critical effects of the process variables required to obtain a good polished surface. Basically, the electrolytic cell consists of specimen anode, cathode and a suitable electrolyte that is usually agitated.

An ideal curve of cell voltage versus current density is shown in fig. 6. The distinct regions of the curve are: A-B which is the region of etching, B-C is the unstable region where periodic oscillation of current is seen. C-D is the polishing region where the polishing occurs at constant current density usually called "limiting current density", D-E is the region where slow gas evolution with pitting occurs and E-F is the region of polishing with rapid gas evolution. A study of good polishing process involves understanding of the influence of variables on the cell voltage-current density relationship, particularly on limiting current density.

Among the electro-polishing variables some are considered as primary variables as their influence is much more significant than that of the secondary variables mentioned. Considering the importance of the primary variables, the present paper discusses in detail the effect of primary variables on limiting current density to obtain a good polished surface.

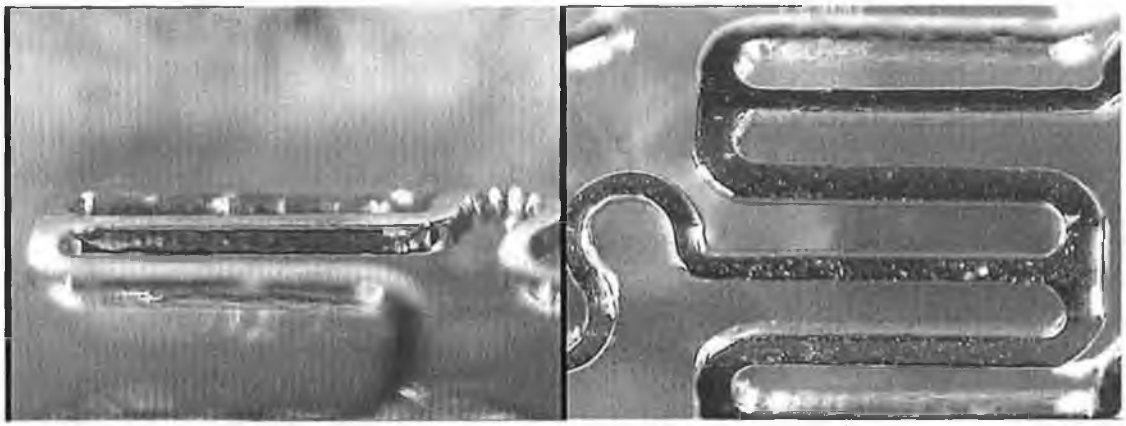


Fig. 7 Electropolished surfaces of a Large Vessel Stent

3.1 Effect of Process Variables on Current Density-Voltage Relationship

Electrolyte (bath) temperature

As the temperature of the bath rises, its resistance decreases and the potential required to produce the limiting current density decreases^{2}.

Stirring of Electrolyte

Stirring the electrolyte during polishing increases the limiting current density and also the specimen is polished better if it is moved through the solution at a moderate and steady speed. It is interesting to note that stirring the electrolyte is expected to disturb the viscous layer thereby will aid the movement of the ions form the specimen anode into the electrolyte towards the cathode and may improve the quality of the polishing. From these observations it has been concluded that the electro-polishing process is a diffusion controlled process^{3}.

Concentration of electrolyte

An increase in concentration of the electrolyte increases the limiting current density at a given voltage. Honeycombe and Hughans [4] have reported that, during electro-polishing of copper specimens using orthophosphoric acid electrolyte at room temperature, limiting current density of 0.04 A/cm^2, whereas, at higher and lower values of limiting current the polishing quality is not good.

Surface Roughness

The contour of the specimen surface is assumed to have peaks and valleys and current density ant the peaks is higher than in the valley[3]. It has been reported that the smoothening during polishing occurs due to the difference on concentration gradient in the viscous layer over the peaks and valleys. At peaks, the layer is thin and the concentration gradient is higher while in the valley the layer is thicker and the concentration gradient is lower. Thus the surface is smoothened due to the preferential attack on the peaks.

Electrode distance

During electropolishing and etching, distance between electrodes (anode and cathode) plays a vital role to identify the optimum limiting current density value (horisontal plateu in the current density-voltage curve).

Polishing Time

Generally, polishing time decreases with decrease in roughness of the specimen surface. But lack of concentration gradient and uniform current density on a fine surface results in a relative slow increase in metal ion concentration around the anode. Thus the establisment of a polishing condition on a very smooth surface requires more time than that of a rough surface.

Viscosity of the Electrolyte

Viscosity of the electrolyte varies in the presence of moderators such as glycerol etc., which significantly affect the limiting current density, consequently polishing. Hickling and Higgins[3] have observed that limiting current density is inversly proportional to the viscosity of the electrolyte.

Cell voltage

The selected supply voltage for good polishing should be well within the voltage range obtain from the current density-voltage curve corresponding to the limiting current density of the polishing region (horizontal plateau).

In addition to the primary variables, secondary variables also play a role in obtaining good polishing surface. The main secondary parameters are: ratio of anode to cathode surface area, surface area of the cathode, surface area or the anode, orientation of the anode and cathode in bath, type of electrode, depth of sample below solution surface, washing procedure and age (repeated usage) of the electrolyte. The ratio of anode to cathode surface area should be less than 0.5. Considering the orientation of the two electrodes in the bath, it is suggested that the electrode surface preferably should be parallel to each other to facilitate polishing.

4. Experimental data of etching

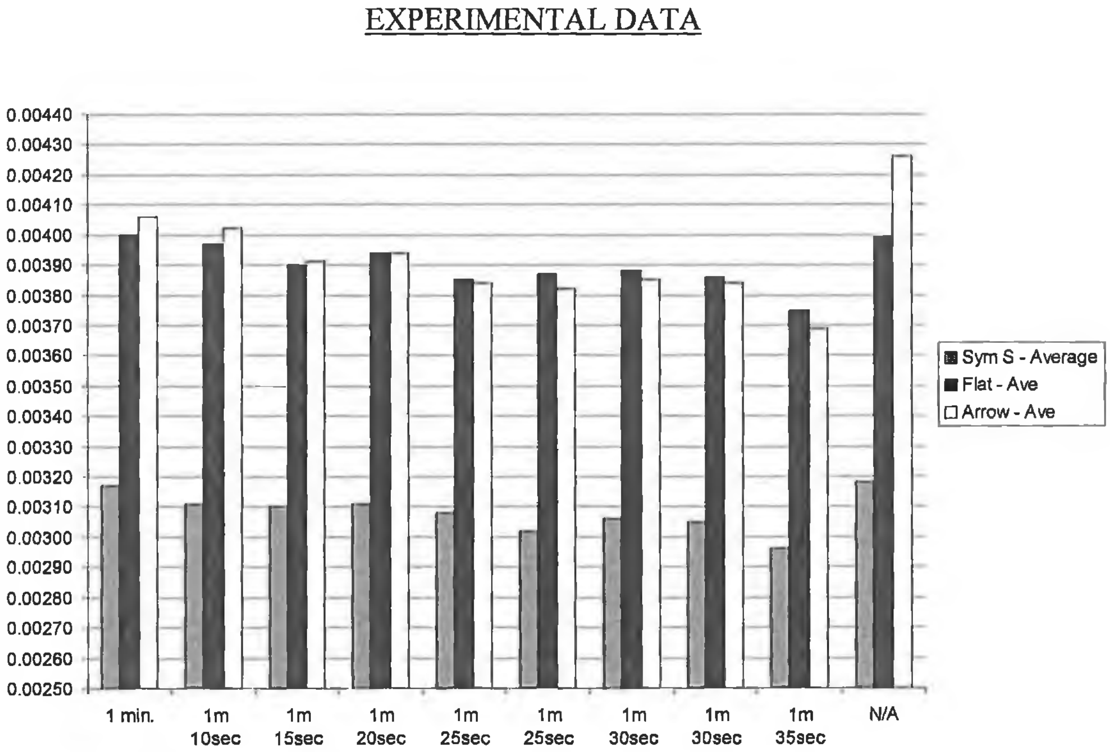


Table 1 – Average Comparation between batches at different parameters

No. Crt	Batch #	Type of stent	Pcs	Etched	Etching Time	Prepolish. Inspection		Symetrical S		Flat		Arrow		Obs.
						Dim insp	Wall thick	Average	Range	Average	Range	Average	Range	
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*10*	*11*	*12*	*13*	*14*	*15*	*16*
1	LB167/11/01	15 mmOC	2	Yes	1 min.	Yes	No	0.00317	0.00056	0.00400	0.00055	0.00406	0.00055	One of them, unacceptable, 2 very clean.
2	LB167/11/02	15 mmOC	2	Yes	1m 10sec	Yes	No	0.00311	0.00071	0.00397	0.00053	0.00402	0.00083	Almost acceptable!
3	LB167/11/06	15 mmOC	2	Yes	1m 15sec	Yes	No	0.00310	0.00055	0.00390	0.00051	0.00391	0.00058	Cleaned. Only one point of crud inside sur.
4	LB167/11/03	15 mmOC	2	Yes	1m 20sec	Yes	No	0.00311	0.00072	0.00394	0.00060	0.00394	0.00079	Clean and acceptable! Very good!
5	LB167/11/04	15 mmOC	2	Yes	1m 25sec	Yes	No	0.00308	0.00057	0.00385	0.00058	0.00384	0.00059	crud inside surface, to be repeaded
6	LB167/11/05	15 mmOC	2	Yes	1m 25sec	Yes	No	0.00302	0.00045	0.00387	0.00071	0.00382	0.00064	Excellent! OK! Very clean!
7	LB167/11/10	15 mmOC	2	Yes	1m 30sec	Yes	No	0.00306	0.00059	0.00388	0.00054	0.00385	0.00069	not cleaned, to be repet it
8	LB167/11/11	15 mmOC	2	Yes	1m 30sec	Yes	No	0.00305	0.00053	0.00386	0.00053	0.00384	0.00060	Very clean! OK!
9	LB167/11/12	15 mmOC	2	Yes	1m 35sec	Yes	No	0.00296	0.00081	0.00375	0.00071	0.00369	0.00076	Very, very clean!
10	LB167/14/13	15 mmOC	5	No	N/A	No	No	0.00318	0.00080	0.00399	0.00066	0.00426	0.00062	HF etched

Table 2 – Etching characteristics of 15 mm Open Cell stents

5. Conclusions

a. Chemical etching is a step which easily can be replaced by electro-etching.
b. There are no disadvantages in electro-etching.
c. Electro-etching can be easily integrated in manufacturing.

Rererences:

1. Pletcher, D., Walsh, F.C. Industrial Electrochemistry. Second edition. 1993, 447-448.
2. Hahn, T.S., Marder, A. R. Effect of electropolishing variables on current density-voltage relationship. Metalography 21, 1988, 365-375
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