

CONTINUOUS VERTICAL CASTING OF Ni-Ti ALLOY, PROPERTIES OF AS-CAST ALLOY FOR MEDICAL APPLICATIONS

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Doctoral Dissertation
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VERTIKALNO KONTINUIRNO LITJE Ni-Ti ZLITINE IN
NJENE LASTNOSTI ZA UPORABO V MEDICINI

Doktorska disertacija

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Abstract

Existing production techniques of commercially available Nitinol (50Ni50Ti) are numerous, complicated and time-consuming. Due to this fact, the aim of the doctoral work was to produce a NiTi alloy in the shape of a rod with the smallest diameter possible in one-step using a combination of Vacuum Induction Melting and Continuous Casting. In these frames, requirements connected to the chemical composition and final properties of the as-cast NiTi rod should fulfilled and they have to be as close as possible to the Nitinol. With the deeper studies, and after many experiments carried out, a 3 m long NiTi rod with diameter 11.5 mm was produced. We found out that the optimal parameters during melting and casting were: 1450 °C melting temperature, 8 mm step, 0,5 s waiting time and 26 l/min mould cooling.

Chemical composition of as-cast NiTi rod was determined with XRF methods and semi-quantitative EDS analysis. Results showed some deviations to the required composition ($\pm 15\%$), which could be attributed to the non-optimised production techniques and measurements' error of the chosen methods. The microstructure of the NiTi rod was observed using Optical and Scanning Electron Microscopy. It was identified that, in the microstructure, there are no visible macro-cracks and or other type of porosity. Detailed microstructure investigations revealed dendritic character, where inside of the dendrites was phase NiTi, and in the inter-dendritic space, NiTi₃ and NiTi phases. Due to the contact between the clay graphite crucible, containing carbon, and the melt of nickel and titanium at high temperature ($> 1450^{\circ}\text{C}$), individual inclusions of titanium carbide were formed. In continuation, the mechanical properties of the as-cast NiTi rod were examined (hardness, tensile, compressive and bending strength). Measurements of the mechanical properties showed that the NiTi rod is hard ($> 550 \text{ HV}$). With the assistance of a tensile, compressive and bending test, it has also been found that the NiTi rod is also brittle, due to the fracture specificity, and that it lies only in the elastic region of the stress-strain curve. As it does not pass into the plastic region, the NiTi rod cannot be strain hardened. Homogenization heat treatment should follow after the CVC procedure.

As the original purpose of the NiTi rod is an application for dental purposes, it was necessary to perform additional tests, which are required for biomaterials. The surface of NiTi rod and commercially available Nitinol, was modified by a layer of titanium oxide (50 nm), which was deposited by the Atomic Layer Deposition technique. Such modified and nonmodified samples were then tested for their biocompatibility with the contact of HUVEC cells, and for their corrosion properties with physiological saline. All tests were performed at body temperature. Results showed that biocompatibility of base NiTi rod, as well as its corrosion properties, are poor in comparison with the commercially available Nitinol. In the case where a layer of titanium oxide was deposited on the NiTi rod, its biocompatibility and corrosion properties were improved considerably.

Povzetek

Obstoječe tehnike izdelave komercialno dostopnega Nitinola (50Ni50Ti) so številne, zahtevne in zamudne. Na osnovi tega dejstva je bil namen doktorske disertacije izdelati NiTi zlitino v obliki palice s čim manjšim premerom in to v enem koraku z uporabo vakuumskega indukcijskega pretaljevanja in kontinuirnega litja. V teh okvirih je bilo potrebno zadostiti nekaterim zahtevam, ki so povezane z doseganjem kemijske sestave in končnih lastnosti odlite Niti palice in to je → da so le-te čim bolj podobne Nitinolu. S poglobljenimi študijami in s številnimi izvedenimi eksperimenti smo uspeli izdelati 3 m dolgo NiTi palico s premerom 11.5 mm. Ugotovili smo, da so optimalni parametri med pretaljevanjem in litjem sledeči: 1450 °C temperature taljenja, korak 8 mm, 0,5 s waiting time and hitrost ohlajanja kokile 26 l/min.

Kemijska sestava odlite NiTi palice je bila določena z XRF metodo in semi-kvantitativno EDX analizo. Rezultati kažejo nekatere deviacije od zahtevane sestave ($\pm 15\%$), kar bi lahko pripisali ne-optimalni tehniki izdelave oziroma merilni napaki pri izbranih metodah. Mikrostruktura NiTi palice je bila raziskana z optično in elektronsko mikroskopijo. V mikrostrukturi ni bilo opaziti vidnih makro-razpok ali drugih vrst poroznosti. Natančnejši pregled mikrostrukture je odkril dendritski karakter, kjer je bila v dendritih identificirana faza NiTi, v med-dendritskem prostoru pa fazi NiTi₃ in NiTi. Zaradi stika med ton-grafitnim loncem, ki vsebuje ogljik in talino niklja in titana so pri visoki temperaturi ($> 1450^{\circ}\text{C}$) nastali posamezni vključki titanovega karbida. V nadaljevanju smo določili mehanske lastnosti (trdota, natezna, tlačna in upogibna trdnost) odlite NiTi palice. Meritve mehanskih lastnosti so pokazale, da je lita NiTi palica trda ($> 550 \text{ HV}$). Na osnovi nateznega, tlačnega in upogibnega preizkusa pa smo ugotovili, da je NiTi palica krhka zaradi specifike zloma, saj se nahaja le v elastičnem področju krivulje napetost-raztezek. Ker krivulja ne prehaja v plastično področje, je NiTi palico nemogoče deformacijsko utrjevati. Dobljeno palico nitinola bi bilo potrebno homogenizacijsko žariti.

Osnovni namen NiTi palice je uporaba za dentalne namene, za to je bilo potrebno izvesti nekatere teste, ki so potrebni pri biomaterialih. Nitinol tvori na zraku ali v tekočinah tanko zaščitno oksidno plast, ki sestoji iz TiO₂ in na ta način preprečuje nadaljnjo korozijo. Na NiTi palico in komercialno dostopni Nitinol smo s pomočjo tehnike nanosa atomskih plasti nanесли tanko plast titanovega oksida (50 nm). Tako modificiranim in nemodificiranim vzorcem smo določili biokompatibilno tanko plast v kontaktu s HUVEC celicami in njihove korozijske lastnosti v fiziološki raztopini. Vsi testi so bili narejeni pri telesni temperaturi. Rezultati testov biokompatibilnosti, kot tudi korozijske lastnosti kažejo, da ima NiTi palica slabše lastnosti od komercialno dostopnega Nitinola. V primeru, ko je bila na površino NiTi palice nanescena plast titanovega oksida, so se njena biokompatibilnost in korozijske lastnosti precej izboljšale.

Contents

Acknowledgments	v
Abstract	vii
Povzetek	ix
List of Figures	xiii
List of Tables	xv
Abbreviations	xvii
Symbols	xix
Introduction	1
1.1 Motivation	1
1.2 Hypotheses	2
1.3 Research Objective.....	2
Scientific Background	3
2.1 Biocompatible Materials	3
2.1.1 Titanium Alloys.....	4
2.2 Ni-Ti Alloys	5
2.2.1 Nitinol Oxidation.....	7
2.3 Nitinol Manufacturing.....	9
2.3.1 Melting	9
2.3.2 Forming of Nitinol.....	11
2.3.3 Secondary Processing Methods	11
2.3.4 Finishing Techniques.....	12
2.4 NiTi Alloys Casting	13
2.4.1 Continuous Casting.....	13
Materials and Methods	15
3.1 Materials.....	15
3.2 Continuous Vertical Casting of NiTi Alloy	15
3.3 Sample Preparation	17
3.4 Microstructure Investigation	18
3.5 Mechanical Properties of CVC NiTi Rod	18
3.6 Atomic Layer Deposition of TiO ₂ Layer	20
3.7 Biocompatibility.....	21
3.8 Corrosion Tests	22
Results and Discussion	23
4.1 VIM Batch Casting of NiTi Alloy.....	23
4.2 Continuous Vertical Casting of NiTi Alloy and its Microstructure	25
4.2.1 Microstructure of CVC NiTi Rod.....	28
4.2.2 Microstructure of Commercially Available NiTi Alloy	32
4.3 Mechanical Properties of As-Cast CVC NiTi Rod	34
4.3.1 Vickers Hardness.....	34
4.3.2 Tensile Test.....	36
4.3.3 Compressive Test	37
4.3.4 4-point Bending Test	38
4.4 ALD TiO ₂ Thin Layer Deposition.....	39
4.5 Biocompatibility of CVC NiTi Rod	42
4.6 Corrosion Tests	46

4.6.1	Potentiodynamic Test.....	46
4.6.2	Electrochemical Impedance Spectroscopy.....	47
Conclusions		53
5.1	Summary	53
5.2	Future Work	54
5.3	Contribution to Science	54
References		55
Bibliography		61
Publications Related to the Thesis.....		61
Journal Articles.....		61

List of Figures

Figure 1: Ni-Ti phase diagram	5
Figure 2: Shape memory effect	6
Figure 3: Model of oxide scale formation on a metallic surface	7
Figure 4: Ti-O phase diagram	8
Figure 5: Pilot VIM furnace	10
Figure 6: VAR furnace .	10
Figure 7: Electron beam melting furnace	11
Figure 8: Vacuum Induction Furnace with mechanism for Continuous Casting.	15
Figure 9: Temperature heating regime by Vacuum induction melting	17
Figure 10: Schematic presentation of copper mould with cooling system.....	17
Figure 11: Thermal Field Emission SEM JSM-6500F.....	18
Figure 12: Instron Tukon 2100B for Vickers hardness measurement	19
Figure 13: INSTRON 1255, 500 kN device for mechanical tests	19
Figure 14: A sample for a) tensile test and b) compressive test.....	19
Figure 15: A sample for 4-point bending test.	20
Figure 16: Steps by ALD deposition.....	20
Figure 17: Beneq TFS 200 system for Atomic Layer Deposition	21
Figure 18: a) Clay-graphite crucible and b) the correct sequence of filling up	24
Figure 19: a) Optical microscope image at 1000-x magnification and b) SE image	25
Figure 20: a) CVC NiTi rod and b) longitudinally macroscopic image	27
Figure 21: Optical microscope image of CVC NiTi rod at 50× magnification.....	28
Figure 22: a) Secondary electron image and b) backscattered electron image	30
Figure 23: a) Points where EDS analysis was made and b) EBSD analysis	31
Figure 24: a) SE image of CVC NiTi rod at 5000× magnification	32
Figure 25: a) Optical microscope image and b) SE image	33
Figure 26: a), b) and c) Elemental mapping at the microstructural level	34
Figure 27: Cross-section of CVC NiTi rod.....	35
Figure 28: Diagram of Vickers hardness for CVC NiTi rod with the distance r.	35
Figure 29: A test specimen of CVC NiTi rod before and after the tensile test.	36
Figure 30: Stress-strain curve for tensile test of CVC NiTi rod.....	37
Figure 31: A test specimen of CVC NiTi rod before and after compressive test.....	38
Figure 32: Stress-strain curve for compressive test of CVC NiTi rod.....	38
Figure 33: A test specimen of CVC NiTi rod before and after the 4-point bending test.	39
Figure 34: : Stress-strain curve for 4-point bending test of CVC NiTi rod.....	39
Figure 35: Secondary electron image at 200000× magnification of cross-section.	40
Figure 36: Secondary electron image at 20000× magnification of TiO ₂ layer.....	41
Figure 37: XPS spectra of TiO ₂	42
Figure 38: Number of adhered HUVEC cells on the surface.....	43
Figure 39: Number of dead HUVEC cells on the surface.....	44
Figure 40: Optical microscope images of HUVEC cells	45
Figure 41: Covered surface area with HUVEC cells	45
Figure 42: Potentiodynamic curves.....	47
Figure 43: Nyquist diagrams.....	50
Figure 44: Equivalent circuits.	51
Figure 45: Total corrosion resistance vs time for different samples.	52

List of Tables

Table 1: Example of parameters used by CVC experiment.	26
Table 2: Results of EDS analysis.	31
Table 3: Percentage of viable HUVEC cells	43
Table 4: Electrochemical parameters determined from the potentiodynamic curves.	46
Table 5: Porous corrosion resistance R_1 and oxide corrosion resistance R_2	51

Abbreviations

VIM	... Vacuum Induction Melting
CC	... Continuous Casting
CVC	... Continuous Vertical Casting
HUVEC	... Human Umbilical Vein Endothelial Cells
etc.	... et ceterum
at. %	... atomic percentage
NiTi	... Nickel - Titanium
nm	... nanometer
TiO ₂	... Titanium Dioxide
mm	... millimeter
Å	... ångström
ZrO ₂	... zirconia
Y ₂ O ₃	... yttria
mbar	... millibar
kW	... kilowatt
kHz	... kilohertz
kV	... kilovolt
nA	... nano-ampere
N	... Newton
TiCl ₄	... Titanium Tetrachloride
H ₂ O	... water
HCl	... Hydrochloric acid
eV	... electron volt
UV	... ultraviolet

Symbols

E_{corr}	... Corrosion Potential
I_{corr}	... Corrosion Current
v_{corr}	... Corrosion Rate
E_{bd}	... Breakdown Potential
I_{bd}	... Breakdown Current
R_{1CVC}	... Porous layer resistance for CVC NiTi rod
R_{2CVC}	... Oxide layer resistance for CVC NiTi rod
R_{1com}	... Porous layer resistance for commercial NiTi
R_{2com}	... Oxide layer resistance for commercial NiTi
$R_{1TiO_2/CVC}$	... Porous layer resistance for CVC NiTi rod with TiO ₂ layer
$R_{2TiO_2/CVC}$	... Oxide layer resistance for CVC NiTi rod with TiO ₂ layer
$R_{1TiO_2/com}$	... Porous layer resistance for commercial NiTi with TiO ₂ layer
$R_{2TiO_2/com}$	... Oxide layer resistance for commercial NiTi with TiO ₂ layer
R_p	... Polarization or totally corrosion resistance

Chapter 1

Introduction

1.1 Motivation

Nitinol is a group of nearly equi-atomic alloys composed of nickel and titanium. It exhibits a unique combination of good functional properties and a high mechanical strength, such as superelasticity and a shape-memory effect, good corrosion resistance in a chloride environment, an unusual combination of strength and ductility, high tendency for self-passivation, paramagnetic properties, high fatigue strength, low Young's modulus and excellent bio-mechanical compatibility [1-7].

This alloy was developed in the 1970s and its properties have enabled its use, especially for biomedical purposes, first in orthodontic treatments, and later on in cardiovascular surgery for stents, guide wires, filters, etc., in orthopaedic surgery for various staples and rods, and in maxillofacial and reconstructive surgery. In addition to bioengineering, nitinol has been used in aerospace, automotive, marine, chemical industries, civil and structural engineering [1-7].

Nitinol manufacturing is a very complex process. Titanium has a high melting point, low fluidity (high viscosity), and a susceptibility to oxidize at high temperatures. These properties make it and its alloys difficult to cast. All nitinol alloys go through similar steps of fabrication. These steps are melting (vacuum melting techniques), forming, secondary processing methods and finishing techniques [8-10].

Casting is pouring molten metal into a mould of the desired shape, and allowing it to go solid [11]. Due to a high concentration of Ti (50 at.%), molten nitinol is highly reactive and must be processed in a vacuum or inert atmosphere to ensure the purity of the product. Vacuum induction melting (VIM) and vacuum arc melting (VAR) processes are commonly used for the production of nitinol [9-10]. After the melting of nitinol, its microstructure must be refined by additional deformation processes to achieve the desired properties [9-10]. Furthermore, it is necessary to utilize further operations to create finished components with the desired shape, properties and to incorporate those components into useful tools and devices [9-10].

All these operations are usually separated, but for greater efficiency the first two steps can be joined into so-called continuous casting. Continuous casting is a manufacturing process where molten metal is solidified into a semi-finished product [11, 12].

Our goal is to successfully determine the production technology of 50Ni50Ti rod. For this purpose, a combination of Vacuum Induction Melting (VIM) and Continuous Casting (CC) in the vertical direction (this combination will be simply called Continuous Vertical Casting (CVC)) was used. Commercially available nitinol is now manufactured using a classic casting method that produces large blocks of solidified nitinol, which is then difficult to prepare (special tools are needed) for further operations, with which nitinol gains some functional properties. We want to obtain nitinol in just one step, which would have similar properties to that which is already on the market.

In this doctoral work we produced a NiTi rod using continuous vertical casting. Mechanical properties, biocompatibility and corrosion resistance were determined for the as-cast NiTi rod. Biocompatibility and corrosion resistance were also determined for the as-cast NiTi rod with a 50 nm TiO₂ layer deposited on its surface. The properties were compared to commercially available nitinol.

Preliminary research has shown the possibility of new production process of nitinol, which is a well-established material in biomedicine, in an attempt to shorten the conventional production of nitinol.

1.2 Hypotheses

The first hypothesis of this doctoral thesis, based on the state of the art, is that continuous vertical casting of the NiTi alloy is possible. However, in practice there are some limitations, such as:

- the reactivity of titanium with practically all the elements,
- high viscosity and consequently poor miscibility of the alloy
- problem of materials which are in contact with the alloy,
- the problem of cooling rate and the achievement of the desired microstructure,
- technological parameters of continuous casting: time of draw and pause by drawing of rod,
- providing the state without breaking the rod
- inhomogeneous/inadequate chemical composition of obtained rod in cross-section.

The second hypothesis is that if we are able to produce with CVC a NiTi rod that has similar chemical composition to commercially available nitinol (50Ni50Ti), then the biocompatibility and corrosion resistance of both should be in the same range.

The third hypothesis is that if we deposit a 50-nm TiO₂ layer on the surface of CVC NiTi rod, the biocompatibility and corrosion resistance of it improves.

1.3 Research Objective

Methods for confirmation of hypotheses are:

- Continuous vertical casting of NiTi alloy in the form of a rod.

Continuous casting of NiTi alloy is not a well studied field due to the high reactivity of titanium (low pressure in the furnace is required or in other words a high vacuum), high viscosity of titanium in liquid form (stirring of the melt is very complicated due to the difference in densities between Ni and Ti), and the alloy is due to the good mechanical properties that are inadequate for secondary processing. We accomplished the continuous vertical casting of the NiTi alloy. We loaded a vacuum induction furnace with raw materials and after melting, the alloy was, with the assistance of gravity and a computer-controlled drawing mechanism, moved out of the furnace to a water-cooled mould where a rod with a thickness of 11 mm was drawn.

- Determination of chemical composition and microstructure of the NiTi rod.

Chemical composition of the as-cast rod was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray fluorescence spectrometry (XRF). The microstructure and containing phases of the as-cast rod were determined by light microscopy and scanning electron microscopy (SEM), equipped with Energy-Dispersive X-Ray Analysis (EDS).

- Determination of mechanical properties of NiTi rod.

On the as-cast rod tests of mechanical properties (Vickers hardness, tensile, compressive and 4-point bending test) were carried out, which indicated elasticity, toughness and hardness of the rod.

- Deposition of TiO₂ layer, biocompatibility and corrosion measurements.

With Atomic Layer Deposition (ALD) we deposited a layer of titanium oxide on the surface of the as-cast rod, because we were interested in the improvement of corrosion properties and biocompatibility if the as-cast rod had a layer of titanium oxide on its surface. The formation of titanium oxide was confirmed by X-Ray Photoelectron Spectroscopy (XPS). Because the material is intended for medical applications, we investigated the behaviour of the as-cast rod in a simulated body fluid, where we studied the corrosion resistance. The biocompatibility of the as-cast rod was as well determined. All the experiments were also made with a commercially available nitinol, which was already in the rolled state.

Chapter 2

Scientific Background

2.1 Biocompatible Materials

Biocompatible materials can be defined as synthetic or natural biomaterials that are continuously or occasionally in contact with body fluids and can partially or totally replace any failing tissue, organ or function of the body in order to improve the quality of life of the individual [13-15]. To successfully employ implants in the human body, a suitable level of tolerance of the material used within the living organism is required. In other words, a high grade of implant biocompatibility is required. Biocompatibility has been defined as “the ability of a material to perform an appropriate host response in a specific application”. Biocompatibility involves the acceptance of an artificial implant by the surrounding tissue and by the body as a whole. Biocompatible materials do not irritate surrounding structures, do not provoke inflammatory or allergic response and do not cause cancer. The most important is the biocompatibility of the surfaces because the surface is directly exposed to the living human tissue. Therefore, it is necessary to tailor the exposed surfaces in view of their chemical, physical, biological and morphological features [13-15].

In general, biomaterials can be divided into the following categories: metals, polymers, ceramics, composites, and biodegradable materials. Metals are inorganic materials possessing metallic bonds with highly mobile electrons. As a result of their ability to conduct electricity, metals are strong and can be relatively easily formed into complex shapes. Metals are used as biomaterials due to their excellent electrical and thermal conductivity, good mechanical properties and corrosion resistance. Metals are most widely used for load-bearing implants. Typically employed metallic biomaterials are stainless steels, commercially pure titanium, titanium alloys, and cobalt-based alloys [5, 13, 15, 16]. Ceramics are inorganic, polycrystalline materials possessing ionic or covalent bonds, which are generally formed at elevated temperatures. Ceramics are very hard and more resistant to degradation in many more environments than metals but they are quite brittle. Ceramics are often used as a part of orthopaedic implants or as dental materials due to their resemblance in chemistry with that of native bone. Ceramics are also used as bearing balls in artificial joints or as bone conductive coatings on metal-based implants because of their abrasive strength. The most commonly used biocompatible ceramics are alumina, zirconia, calcium phosphates, bioactive glasses and glass ceramics [13, 14, 16]. Polymers are organic materials possessing long chains with a large number of small repeating units (monomers) that are held together by covalent bonds. The main advantages of the polymeric biomaterials compared to metal or ceramic materials are the ease of manufacturability to produce various complex shapes, ease of surface properties improving, ease of secondary processability, reasonable cost and availability with desired mechanical and physical properties. The critical issue of polymeric biomaterials is that they easily absorb water and biomolecules from the surroundings and can thereby alter the surface chemistry. On the other hand, polymers are, in comparison to metals or ceramics, soft materials that may undergo mechanical wear and breakdown [13, 16]. Composites are materials in which the distinct phases are separated on a scale larger than atomic and in which properties such as the elastic modulus or hardness are significantly altered and improved in comparison with those of a homogeneous material. It is important that each constituent of the composite is biocompatible. The most successful composite biomaterials are used in the field of dentistry as restorative materials or dental cements [15, 16]. Biodegradable materials are materials that could be destroyed by nature through hydrolytic mechanisms. The main advantage of biodegradable materials is that they do not cause permanent chronic foreign-body reactions due to the fact they are gradually absorbed by the human body and do not permanently leave traces of residual material in the implantation sites. Degradable implants

made of metal are considered as a novel concept. In terms of mechanical properties biodegradable metals are more suitably compared to biodegradable polymers when a high strength-to-bulk ratio is required, such as for internal bone fixation screws and coronary stents. Magnesium- and iron-based alloys are two classes of metals that have been proposed [16, 17].

The reliability of the biomaterials in the body environment depends on factors such as material properties, design, biocompatibility, and operation technique and health condition of the patient. Implants are intended to be in use for a long period of time inside the body. Tissue response to biomaterials depends on mechanical properties of structural biomaterials in a living body environment, such as fatigue, toughness, wear and corrosion resistance [14, 18, 19]. Corrosion is the unwanted chemical reaction of a metal with its environment, resulting in its continued degradation to oxides, hydroxides or other compounds. Tissue fluid in the human body contains water, dissolved oxygen, proteins, and various ions such as chloride and hydroxide. As a result, the human body presents a very aggressive environment for metals used for implantation [14]. A consequence of corrosion and the lack of a protecting layer is also the increased diffusion of ions that can be harmful for the surrounding tissue [17]. Fatigue is damaging or weakening of the material. It is important to determine the fatigue characteristics of implants, because it is expected that the chosen material will bear numerous cyclic loadings without failure or fracture for a long period of time. Fatigue characteristics are closely related to the microstructure of the metallic phases and therefore also with the processing and heat treatment employed [17, 18]. Wear is the displacement of material from its original position as a result of interactions between more surfaces. More specifically, wear is about the removal of the dense oxide film that is naturally formed on the surface of metallic implants [17].

2.1.1 Titanium Alloys

The α -phase titanium has at low temperatures close-packed hexagonal crystal structure which at 882 °C transforms to a body-centred cubic β -phase that remains stable to the melting temperature (1670 °C). Some alloying elements increase the alpha-to-beta transition temperature (alpha stabilizers), while others lower the transition temperature. The α -phase stabilizers are Al, C, N, O, Ga, Ge, and the β -phase stabilizers are Mo, V, Ta, Nb, Mn, Fe, Cr, Co, Ni, Cu and Si [5].

Titanium and its alloys have the highest bio-tolerance among all currently applied metallic biomaterials, good crevice and corrosion resistance in a chloride environment, high tendency to self-passivation, paramagnetic properties, high fatigue strength and the lowest Young's modulus of all metallic biomaterials. Their elastic modulus is approximately half of that of stainless steels and therefore creates less risk of stress protection of bone [5]. The success of Ti as implant material is related to its ability to osseointegrate into the surrounding bone, meaning that it exhibits bioactive properties in the presence of tissue, allowing the growth of bone directly up to its surface. The reason for the success of Ti implants is that Ti is a highly reactive metal that forms a dense, coherent passive oxide film, which prevents the progress of corrosion products into the surrounding tissues in the initial stages of implantation. Titanium and its alloys are more expensive than stainless steels and their wear characteristics are poor so they are not suitable for load-bearing surfaces [5, 13].

Titanium and its alloys have a tendency for self-passivation in a physiological saline solution. The passive films formed on the surface consist mainly of amorphous titanium dioxide. However, naturally formed oxides on the metal surfaces are thin and do not form a direct chemical bond with bone tissue, which limits the strength of bonding. Bonding has been improved with formation of hydroxyapatite layer on the titanium surface. By applying an appropriate electrolyte and anodic oxidation, it is possible to incorporate calcium, phosphorus and silicon into the oxide layer of titanium. The Ca and P ions (formation of apatite) contained in the solution penetrate the inside of the porous oxide layer. The oxide layer enriched in this way is characterized by an increased biocompatibility. Chemical treatment in alkali solutions is an effective method to prepare bioactive titanium metals for medical applications. Titanium alloys such as Ti6Al4V (90 at.% Ti, 6 at.% Al and 4 at.% V) form a bioactive graded structure of sodium titanate on their surfaces by the NaOH and heat treatment. The main goal of this alkali treatment is to create a sodium titanate layer that can induce apatite formation by providing surface functional sites composed of Ti–OH groups which are effective for apatite nucleation [6, 20-24].

The mis-match of Young's modulus of the human bones and Ti alloys lead to stress shielding effects responsible for bone resorption and the eventual loosening of implants. Porous structures are expected to provide a better interaction with the bones due to their lower elastic modulus. The use of porous Ti and Ti6Al4V alloy implants allows a higher degree of bone in-growth and body fluid transport through three dimensional interconnected arrays of pores promoting the interactions between the bone and the implant. Pores improve the bone-tissue formation by

allowing the migration and proliferation of osteoblasts and mesenchymal cells. In addition, a porous surface provides mechanical interlocking between the implant and the surrounding bone, enhancing mechanical stability at the interface [25-28].

The commercially most used titanium-based implant materials are pure titanium and Ti6Al4V because of their excellent combination of biocompatibility, corrosion resistance and mechanical properties. New types of alloys like Ti6Al7Nb and Ti5Al2.5Fe have been, however, recently developed due to the toxicity of the alloying elements (V, Al) and high elastic modulus of previously used alloys as compared to that of bone [29-31].

2.2 Ni-Ti Alloys

The binary Ni-Ti alloy system (Figure 1) reveals a very complex and wide range of interactions between nickel and titanium. The nearly equi-atomic Ni-Ti alloys, where the boundary of NiTi on Ti-rich side is nearly vertical and the boundary on the Ni-rich side decreases with decreasing temperature greatly, reveal several interesting characteristics, such as shape memory, superelasticity and corrosion resistance and is therefore the most interesting to research. The alloy in this region is called nitinol (NiTi). Nitinol is a group of nearly equi-atomic (50 at.% Ni and 50 at.% Ti) NiTi shape-memory alloys. It is well known for its properties like shape-memory effect, superelasticity with large recoverable strain, high tensile strength, good fatigue and corrosion resistance and biocompatibility [32-36].

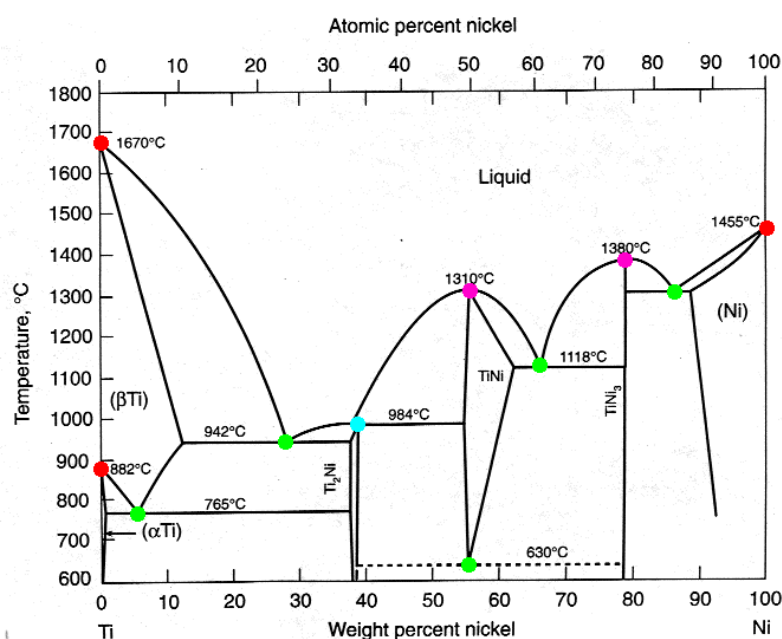


Figure 1: Ni-Ti phase diagram [37].

Nitinol alloys exhibit two closely related and unique properties: shape-memory effect and superelasticity. Pseudoelastic (or superelastic) NiTi is capable of recovering large inelastic strains spontaneously upon unloading. On the other hand, shape memory is exhibited when NiTi recovers large strain deformation upon heating. Both the superelasticity and shape-memory effect are induced in nitinol by reversible, displacive, diffusionless, solid-solid phase transformations from a high-temperature parent phase (austenite) with highly ordered crystal structure (simple cubic, B2) to a low-temperature, stress-free martensite that has a less ordered structure (B19', monoclinic). Another intermediate phase that sometimes appears is called the R phase, which is a rhombohedral distortion of the B2 structure. Nitinol is hysteretic, and there are several transformation temperatures, including the austenite start temperature (A_s), the austenite finish temperature (A_f) during heating and the martensite start temperature (M_s) and the martensite finish temperature (M_f) during cooling. Additionally, an intermediate phase (R phase) often appears during cooling, having its own start temperature (R_s) and finish temperature (R_f), before the transformation proceeds to martensite at lower temperatures. The shape-memory effect (Figure 2) is a temperature-dependent phase transformation. Nitinol's elastic response is followed by a

stress-induced phase transformation from a cubic, austenite phase to a monoclinic, martensite phase that can result in fully recoverable macroscopic strains as high as 8% or more. On unloading, the martensite becomes unstable and transforms back to austenite, with an accompanying macroscopic strain recovery. However, superelastic behaviour will only occur if the material is loaded above its A_f temperature. When loaded in the temperature range $M_s < T < A_f$, stress-induced martensite can form only the elastic deformation of the martensite lattice. If the material is heated in this condition to a temperature above A_f , the deformation is recovered. This is the shape-memory effect. Above the M_d temperature, stress-induced martensite will not form and Nitinol behaves like a conventional engineering material with the material exhibiting linear elastic and plastic regions, before ultimate failure. At this temperature, which is much greater than A_f , the critical stress required to form martensite is greater than that required to drive dislocations, resulting in plastic deformation and the loss of the material's superelasticity. Shape-memory properties are strongly dependent on alloy composition and is therefore crucial to produce alloys with a good chemical homogeneity; it is known that a difference of 0.1 at.% in Ni-content results in a 10 K difference in phase-transition temperatures. The temperature range within nitinol is superelastic includes human body temperature [2, 3, 38-40].

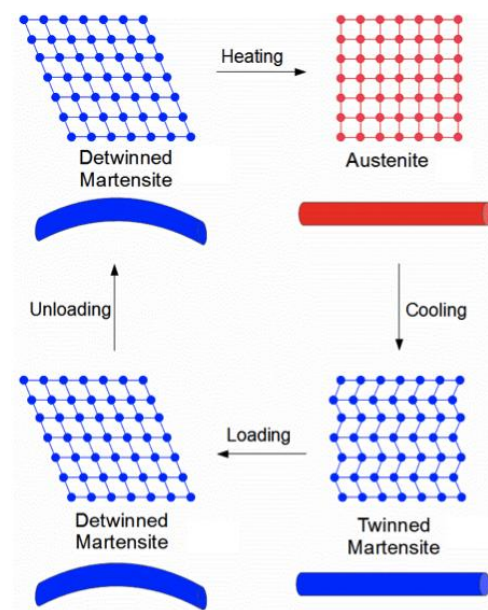


Figure 2: Shape memory effect [41].

The main problem of nitinol is high Ni content. Ni releasing can induce toxic, allergic and hypersensitive reactions or tissue necrosis after long term implantation. Leaching of Ni can arise when a strongly acidic fluid attacks the surface of the alloy. This corrosion is accompanied by nickel release from an implant into the surrounding body fluid and tissue, which can enhance an allergic reaction in a sensitive organism. Second, corrosion can cause pitting and a reduction of mechanical performance of an implant. In an extreme case, an implant broken due to corrosion might produce sharp fragments that are dangerous for the surrounding tissue. Another path leading to the accumulation of Ni in the surface layers can be the type of surface treatment itself. Low-temperature (60–160 °C) pre-treatment protocols or high-temperature annealing in air used for deposition of thick TiO_2 layer onto nitinol surface results in Ni accumulation in the surface depth. This hidden Ni can be easily released through the defective surfaces, exceeding the Ni release from non-treated material by two to three orders of magnitude. A high concentration of Ni close to the metal–oxide interface will yield larger particles. The larger particles will induce severe local strain in the lower oxide layer, leading to local rupture and cracking. Such cracks can then extend towards the surface and act as channels, explaining the much greater Ni release. To prevent corrosion and consequently Ni release, a coating of appropriate thickness must be formed on the NiTi surface. Titanium oxide coatings are useful enough to suppress nickel ions outleaching [33, 34, 42-44].

Nitinol is a promising material for surgical implants in orthopaedics. It is useful as orthodontic archwires due to superelasticity that exerts gentle and retentive force to teeth, which is superior

over stainless-steel wires. Shape-memory bracelets do not require as frequent visits to the dentist as the classic ones because of their ability to self-adjust. The therapeutic period is therefore cut down by 50 %. NiTi is also attractive for atrial septal occlusion devices, stents, which are generally utilized to restore a damaged blood vessel, for bone fixators (bone clamps, plates, wires and pins), dental and laparoscopic devices [34, 42, 45-47].

2.2.1 Nitinol Oxidation

Oxidation is a special form of corrosion degradation of metals and alloys that occurs when the metals or alloys are exposed to air, oxygen or in other environments, such as sulphur dioxide and carbon dioxide, which have relatively low oxidation potentials. The degradation is generally in the form of oxide scale formation. If the formed oxide scale is thin, slow growing, and adherent, it protects the substrate from further oxidation. However, if the scale spalls frequently, the metal is consumed continuously and the material ultimately fails [48].

Thermodynamically, an oxide will form on the surface of a metal when the oxygen potential in the environment is greater than the oxygen partial pressure in equilibrium with the oxide. This equilibrium oxygen pressure is determined from the standard free energy of formation of the oxide:

$$\Delta G^\circ = -RT \ln p(a_{MO_2} / a_M p(O_2)) \quad (1)$$

where a_{MO_2} and a_M are the activities of the oxide and the metal, and $p(O_2)$ is the partial pressure of the oxygen gas. Assuming unit activity of the solid constituents (metal and oxide), Equation 2 becomes [48]

$$\Delta G^\circ = RT \ln p(O_2) \quad (2)$$

or

$$p(O_2) = \exp(\Delta G^\circ/RT). \quad (3)$$

Thermodynamics only tells us whether oxide formation is possible under certain conditions of temperature and partial pressure of oxygen. Sometimes it is possible that the kinetics of the process are so slow that even if there is a possibility for the reaction to occur thermodynamically, it will take very long to form. Thus, it appears that the oxidation reaction has not occurred. Reaction rates and the corresponding rate equations for the oxidation of a metal depend upon a number of factors. The most important are temperature, oxygen pressure, surface preparation, and pre-treatment of the metal [48].

Formation of an oxide scale can be divided into four steps (Figure 3):

- oxygen adsorption at the surface
- oxide nucleation
- lateral growth of the nuclei
- formation of a compact oxide scale [49].

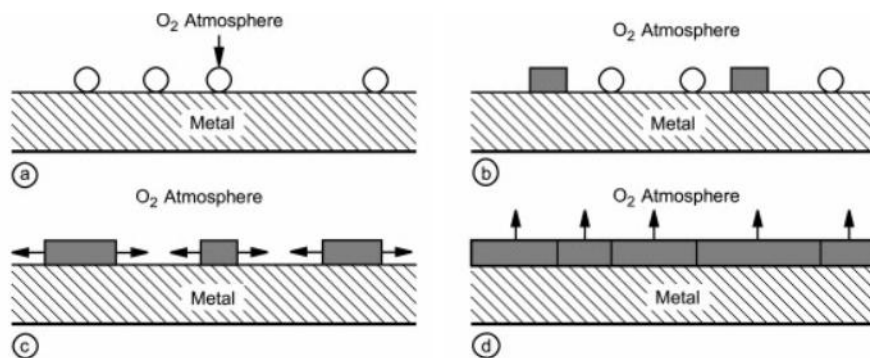


Figure 3: Model of oxide scale formation on a metallic surface [49].

When the lateral growth of the nuclei is concluded, the metal surface is completely covered with a thin oxide film. At elevated temperatures and sufficiently high oxygen partial pressures, steps (a–c) occur very rapidly, hence having only a minor effect on the oxidation kinetics. Once a thin, compact film has been formed on the metal surface, further growth of the oxide scale is controlled by mass transport through the oxide scale. At low temperatures, mass transport is predominantly influenced by grain-boundary diffusion due to its lower activation energy, and by cracks and voids that may provide direct access of oxygen to the metal surface. At elevated temperatures, mass transport can be dominated by volume diffusion [49].

When titanium is subjected to oxidizing conditions, titanium dioxide is formed. Titanium dioxide crystallizes in three major different structures; rutile (tetragonal, $a=b=4.584 \text{ \AA}$, $c=2.953 \text{ \AA}$), anatase (tetragonal, $a=b=3.782 \text{ \AA}$, $c=9.502 \text{ \AA}$) and brookite (rhombohedral, $a=5.436 \text{ \AA}$, $b=9.166 \text{ \AA}$, $c=5.135 \text{ \AA}$). Other structures exist as well, for example, cotunnite TiO_2 has been synthesized at high pressures and is one of the hardest polycrystalline materials known [50]. Oxygen solubility in titanium up to melting temperatures plays an important role in the materials science of titanium alloys, because it contributes to a better understanding of the high-temperature corrosion behaviour of titanium alloys in the fields of their processing and application. According to the now most exhaustive Ti-O phase diagram (Figure 4) the closed-packed hexagonal (hcp) modification of titanium has an extraordinarily high solubility for oxygen up to about 30 mol% in contrast to the high-temperature body-centred cubic (bcc) modification. The bcc modification reaches its maximum of oxygen solubility with 8 mol% at a peritectic equilibrium at $1720 \text{ }^\circ\text{C}$. The hcp phase melts congruently at $1885 \pm 25 \text{ }^\circ\text{C}$ with an oxygen content of about 24 mol%. The titanium-oxygen system has long been important in the study of non-stoichiometry. Rutile, one of the most studied phases of TiO_{2-x} , only exists in nonstoichiometric form and has a complicated defect structure. For low x , the point defects that dominate are oxygen vacancies and titanium interstitials. As the sample is reduced, defect structures with long-range order form – the so-called Magnéli phases. These phases are extended planar defect structures, the crystallographic shear planes that are changing the stoichiometry without relinquishing the cation's primary coordination requirements. This new structural mechanism gives rise to homologous series of phases $\text{Ti}_n\text{O}_{2n-1}$, with $4 \leq n \leq 9$. The higher oxides in this system are distinguished from the lower ones by an internal structural consistency, which strongly influences their properties [51, 52].

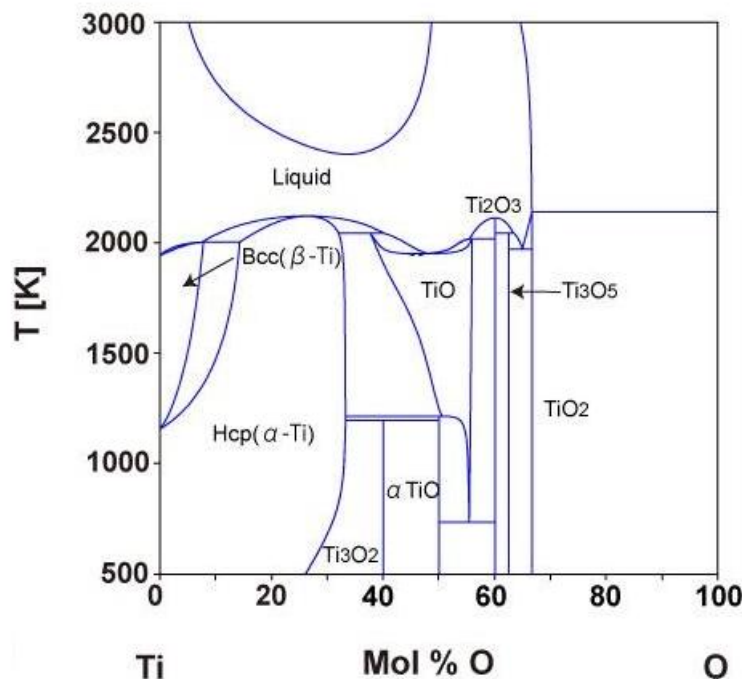
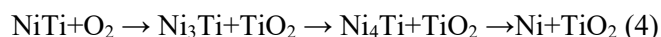


Figure 4: Ti-O phase diagram [53].

TiO_2 is an electron excess conductor with oxygen deficiency. Due to the electroneutrality condition oxygen vacancies must be compensated by a corresponding number of negative

charges. This can be achieved by O^{2-} ions that are incorporated into the lattice resulting in electroneutrality of the complete crystal. The disorder of the oxide determines which species are mobile in the course of oxidation. The driving force for diffusion is the concentration gradient of the vacancies in the oxide such as in TiO_2 oxygen ions diffuse inward since the oxygen vacancy concentration is highest at the oxide/metal interface. The disorder in oxides does not only determine the location for scale growth, but also influences the ability of the oxide scale to the close cracks by oxide re-growth during high-temperature exposure [49].

Oxidation of nitinol occurs as follows:



Due to the four times lower Gibbs free energy of formation of titanium oxide than that of nickel oxide, titanium oxide growth is preferred on nitinol surface. Observations are consistent with a model of oxygen absorption on the $NiTi$ surface that reacts with outward diffusing Ti to form TiO_2 . During the early stages of oxidation, the growth of the TiO_2 layer is the only contributor to thickness and therefore oxide formation is relatively rapid. However, the preferential oxidation of Ti creates a Ti -depleted (Ni -rich) zone at the $NiTi/TiO_2$ interface. The formation of the Ni -rich layer increases the effective diffusion distance with an associated decrease in overall oxidation kinetics. Continued oxide growth therefore involves the simultaneous nucleation and growth of titanium oxides and Ni -rich phases. Ultimately, these processes lead to the formation of a protective oxide scale, which prevents further oxidation of the base material [54, 55]. Naturally grown titanium oxide on a nitinol surface is approximately 5 nm thick and to achieve better properties thicker titanium oxide should be formed. The most common methods employed are anodization, plasma spraying, atomic layer deposition (ALD), etc [13].

2.3 Nitinol Manufacturing

Titanium alloys are corrosion resistant and possess high strength-to-weight ratios. However, titanium has a high melting point, low fluidity, and a susceptibility to oxidize at high temperatures. These properties make it and its alloys difficult to cast. All nitinol alloys go through similar steps of fabrication. These steps are melting (vacuum melting techniques), forming, secondary processing methods and finishing techniques [8-10].

2.3.1 Melting

Due to the high concentration of Ti (50 at.%), molten nitinol is highly reactive and must be processed in vacuum or inert atmosphere to ensure the purity of the product. Vacuum induction melting (VIM) and vacuum arc melting (VAR) and electron beam melting processes are commonly used for production of nitinol. Other melting processes such as cold skull melting and plasma melting are also used in experimental scales [9, 10].

- VIM

In the VIM process (Figure 5), a graphite or calcia (CaO) crucible is preferred. Other crucible materials such as alumina or magnesia contaminate the molten nitinol with oxygen. Molten nitinol picks up carbon contaminant from graphite crucible due to high reactivity of titanium and higher diffusion coefficients at elevated temperature. If the melting temperature is held below $1450^\circ C$ when using a graphite crucible, the carbon content of a VIM nitinol ingot can be controlled between 200 and 500 ppm. The carbon in $NiTi$ alloys forms TiC , increases the Ni -concentration and thus results in a decrease of phase transition temperatures. At the start of VIM process all of the ingredients are placed in an electrically conductive crucible in a vacuum chamber. Then the crucible is heated by electrical induction field which is also stirring the alloy throughout the process, giving a very well-mixed uniform melt. The homogeneity of the product is reached if a transformation temperature consistency within a few degrees is achieved. The molten alloy is then poured into a mould, where it solidifies into a cast ingot [2, 9, 10, 56].



Figure 5: Pilot VIM furnace [57].

- VAR

In the VAR process (Figure 6), consumable electrodes of nitinol are melted and solidified in a water-cooled copper mould. Because there is no contamination from the crucible, cleaner materials with carbon content less than 200 ppm are produced. However, only small amount of ingot is molten at any time and the complete lack of stirring within the entire ingot leads to less homogeneous chemistry and the distribution in transformation temperature when compared to the VIM ingot. Multiple re-melts are required in the VAR process to achieve an acceptable homogeneity. In VAR process, first the base material is pressed into a large compact, which is used as a consumable electrode. An electrical arc is initially struck between the electrode and the bottom of the crucible and sufficient current is passed to continuously melt the electrode. As the material is melted, the electrode is slowly withdrawn as the alloy solidifies at the bottom of the melt pool [9, 10, 56].

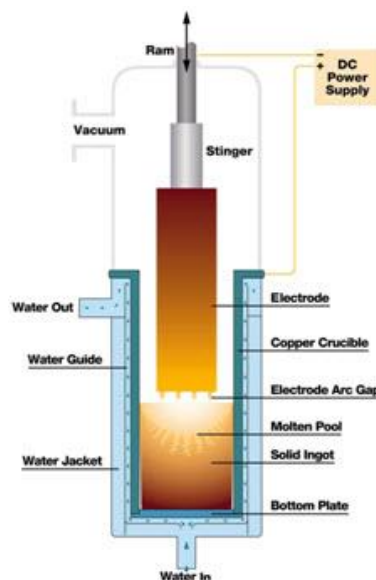


Figure 6: VAR furnace [58].

- Electron beam melting

In the electron beam melting process (Figure 7), the raw material (nickel and titanium) is laterally fed continuously into the path of a vertical electron beam that melts the charge. Simultaneously, the molten product drops into water-cooled copper extractor that is mounted inside the water-cooled copper mould. Carbon and oxygen contamination is minimized because melting is

performed in a water-cooled copper crucible and under a high vacuum. The disadvantage of the EBM process in alloy production comes from the fact that during melting and remelting, it is difficult to control the nominal chemical composition due to the high vacuum operation and heating temperature [56].



Figure 7: Electron beam melting furnace [56].

2.3.2 Forming of Nitinol

After the melting of nitinol, its microstructure must be refined by additional deformation processes to achieve any useful properties. The as-cast microstructure does exhibit a very low quantity of shape memory, superelasticity, fracture resistance and ductility. To achieve suitable microstructure, the nitinol should go through a series of hot and cold working processes [9, 10].

- Hot working

After melting, the nitinol ingot is usually forged and rolled into a bar or a slab at elevated temperatures. Such hot working processes break down the cast structure and improve the mechanical properties. Optimal hot-working temperatures appear to be around 800°C where the alloy is easily workable and the surface oxidation in air is not too severe. The hot-working techniques are forging, rotary forging, extrusion, swaging, bar rolling, rod rolling and sheet rolling [9, 10].

- Cold working

Following hot working, nitinol alloys are cold worked and heat treated to obtain the final dimensions with desired physical and mechanical properties. Cold working of nitinol is quite challenging because the alloy work-hardens rapidly and then it must be fully annealed at 600–800°C. A multiple series of such cold working and annealing steps are required until the final dimension of product is obtained. Cold drawing and cold rolling are the most common processes used. Round wires are produced by die drawing processes. Retaining the surface oxide, nitinol wires can be successfully drawn to small sizes. Lubricants successfully used for the drawing of nitinol wires are sodium stearate soap, molybdenum disulphide, graphite-containing water based lubricant and oil based lubricant. Following a similar reduction schedule, rectangular wires can be manufactured by drawing round wires while flat wires are typically produced by cold rolling [9, 10].

2.3.3 Secondary Processing Methods

After the bulk fabrication of nitinol is completed and nitinol is converted to ribbon, sheet or tubing, it is necessary to utilize further operations to create finished components with the desired shape, properties and to incorporate those components into useful tools and devices. Such techniques are machining, cutting, heat treatment, joining [9, 10].

- Heat treatment

Superelastic nitinol materials are typically heat treated in the vicinity of 500°C, but also lower temperatures in the range between 350°C and 450°C are suitable for shape-memory alloys. Alternatively, for alloys with greater than 55.5 weight percent Ni, good superelasticity and shape-memory effect can be obtained by solution treatment at high temperatures between 600°C and 900°C and subsequent aging at a temperature around 400°C. This aging process induces precipitation hardening of Ni-rich phases. The transformation temperatures are elevated significantly as the matrix composition adjusts during aging [9, 10].

- Machining

Machining is process in which machine tools are used to cut materials to desired sizes and shapes. It is difficult and causes significant tool wear, but nitinol can be machined using conventional techniques such as milling, turning and drilling. Shearing and blanking are quite effective with proper tool design and maintenance. Carbide tools with chlorinated lubricant are recommended for these operations. Abrasive processes such as grinding, sawing and water-jet cutting with abrasive particles are successfully used for nitinol [9, 59].

- Cutting

In addition to the machining operations, there are a number of cutting operations (shearing, abrasive sawing, photochemical etching, laser cutting and waterjet cutting) that are used to separate the components from bulk material, often in a way that simultaneously determines the shape of the finished part [10].

- Joining

Joining is the process of attaching components or structural elements to create an assembly, where only the assembly of components gives some functions that are preferred and cannot be achieved by single element. Welding nitinol to itself has been successfully performed using CO₂ laser. Superelasticity and shape-memory effect are generally well kept in these welding processes, but some degradation in tensile strength and the resistance to permanent deformation was noted. Joining nitinol to dissimilar metals is significantly more challenging. Welding nitinol to stainless steel is especially difficult due to the formation of brittle intermetallic compounds, TiFe and TiFe₂. With proper design and tooling, mechanical joining techniques such as crimping and swaging offer alternatives that can provide reliable joints between nitinol and dissimilar metals [10, 60].

2.3.4 Finishing Techniques

The finishing of nitinol gives it the desired surface condition, appearance, cleanliness and compatibility with its intended use. Some of these operations are cleaning and etching, polishing and coating [9, 10].

- Cleaning and etching

After fabrication bulk nitinol has a surface coatings of oxides, lubricants or contaminants that must be removed. Nitinol is highly resistant to attack by water or detergent type cleaners that remove most contaminants and lubricants, though organic solvents may be needed to clean some lubricants. Caution should be considered when using high concentrations of alkaline cleaners that can lead to embrittlement and pitting of nitinol [10]. Most acids do not attack nitinol at any significant rate due to the inert TiO₂ layer on the surface. It is possible, with a combination of nitric and hydrofluoric acids, to remove oxide layers and then attack the underlying alloy. It is desirable to minimize the time that nitinol is exposed to the acid bath to less than 2 minutes or the possibility of nitinol to pick up hydrogen from the acids and suffer hydrogen embrittlement will increase [10].

- Polishing

With polishing the surface layers that have been affected by cutting or etching are removed. It is also desirable to make round corners and very smooth surface. Nitinol is easily smoothed with the correct abrasive and the natural thin oxide layer protects from damaging and maintains the shiny finish [10].

- Coating

Modification of surface properties by thin-film deposition allows us to create and optimize surfaces with desired chemical and physical properties. The driver for surface modification approaches is that it is often difficult to achieve desired bulk properties of a material, such as

mechanical strength and appropriate surface properties (corrosion resistance, wear resistance, etc.) that provide biocompatibility. In order to improve corrosion, wear and fatigue resistance and to reduce toxic ions release from metallic implant, coating needs to be formed on the implant's surface and the surface should be smooth. The most protective coatings that can be generated are titanium nitride, titanium or chromium oxide, and in the case when the implant is replacing the bone, hydroxyapatite (Ca and P mineral that is the main component of bone) [61, 62]. Titanium and its alloys have tendency for self-passivation in a physiological saline solution. The passive films formed on surface consist mainly of amorphous titanium dioxide. However, naturally formed oxides on the metal surfaces are thin and do not form a direct chemical bond with bone tissue, which limits the strength of bonding. These properties have been improved with the formation of a hydroxyapatite layer or titanium oxide layer on the surface of titanium alloys [6].

2.4 NiTi Alloys Casting

Casting is loading molten metal into a mould of the desired shape, and allowing it to go solid. When the molten metal is loaded into the mould, chill crystals nucleate on the cold walls of the mould and grow inwards. But the chill crystals are soon overtaken by the much larger columnar grains. Finally, nuclei are swept into the remaining liquid and these grow to produce equiaxed grains at the centre of the ingot. As the crystals grow they reject dissolved impurities into the remaining liquid, causing segregation. This can lead to bands of solid impurities or to gas bubbles. And because most metals contract when they solidify, there will be a substantial contraction cavity at the top of the ingot. Casting is a batch process that produces large ingots requiring significant subsequent processing. Large mechanical equipment with high construction and operational costs is necessary to break down most ingots. These problems can be solved by using continuous casting [11, 12].

2.4.1 Continuous Casting

Henry Bessemer suggested a continuous casting method in 1856. Bessemer's idea was to cast molten metal between two water-chilled rolls. The process turned out to be very difficult to control and he only succeeded in producing some small plates of very poor quality. But the process was important for future development. After almost 100 years of experimental work these methods could be used on an industrial scale. In the 1940s continuous casting of non-ferrous metals became a common production method. In 1943 Junghans demonstrated a newly developed process of continuous steel casting on a pilot scale using a vertical machine. Today continuous steel casting is a well-established method. It is the dominating casting process for steels (over 90 % of world production) and aluminium [63, 64].

Continuous casting is a manufacturing process where molten metal is solidified into a semi-finished product. Metal is melted in the crucible and then cast through a mould. The casting travels downwards and its length increases with time. Continuous casting is characterized by high cooling rates which allow a very short time for the diffusion processes and can lead to an extremely fine microstructure that increases the material's toughness. This process is used most frequently to cast steels, aluminium and copper [11, 12, 63, 64].

The advantages of continuous casting compared to ingot casting are:

- the metal yield is often high because only part of the strand has to be cut off and remelted due to pipe formation,
- small casting dimensions can be cast directly with no need for a process like ingot rolling,
- a larger part of the casting work can be mechanized,
- the castings have a more uniform composition than with ingot casting [63].

2.4.1.1 Continuous Casting of NiTi Alloys

Continuous casting of NiTi alloys is today still a much under investigated field. There are some theoretical [65] and numerical [66, 67] researches but no one has yet investigated the continuous casting of NiTi alloys practically. There are some researches about twin-roll casting of NiTi alloys [68-70].

Suzuki H.G. et al. [65] studied the possibility of continuous casting for NiTi alloy. The results showed that dynamic recovery type deformation occurs in the β region resulting in the excellent ductility for NiTi alloy. Continuous casting and hot direct rolling process can be successfully applied to NiTi alloy on condition that cast materials are unbending above the β transus temperature in the conventional continuous casting machine.

Ternik P. and Rudolf R. [66] investigated the numerical analysis of the solidification process of NiTi binary alloy in a lab-scale continuous casting device. The temperature and liquid NiTi mass-fraction distribution has been calculated to study the effect of casting speed. The results showed that the change in casting speed affects the temperature distribution significantly, which affects the solid shell thickness in the copper mould. A high casting speed can cause defects in the final cast. Metallurgical length (i.e., the distance where solidification is sufficiently complete) increases with an increase in casting speed. For high casting speed the metallurgical length exceeds the computational continuous casting domain and NiTi may not become completely solidified at the exit of the mould. Ternik P. et al. [67] also investigated the influence of thermal conductivity on the NiTi solidification process in terms of numerical analysis. The physical medium was taken as an incompressible fluid where the heat was transferred by conduction and convection, including the thermal phase-change phenomenon. The results show that increased thermal conductivity increases the heat-conduction mechanism, widens the solid phase region, increases the solid mass fraction and fastens the solidification process (reduces the solidification time).

The twin-roll casting technique belongs to a family of continuous casting processes, where a solid sheet can be produced directly from the melt. Generally, a molten alloy is ejected into a space between two opposite rotating rollers. The rollers are water-cooled. Firstly, a thin layer solidifies on both surfaces of the rollers. Then the rest of the melt becomes a solid at the solidification endpoint [68]. Goryczka T. and Ochin P. [68] have proved that the twin-roll casting technique appears as a useful method for the NiTi shape-memory alloy manufacturing. The strip showed its structural and chemical homogeneity. Isola L. et al. [69] researched $\text{Ti}_{50}\text{-Ni}_{47}\text{-Co}_3$ strips obtained by the twin-roll casting process. The strips showed a typical solidification structure, where austenite columnar grains tend to be oriented perpendicular to the strip surfaces. The degree of shape recovery reached a value of about 5.5% in thermal cycling under load experiments. Dalle F. et al. [70] have produced $\text{Ni}_{49.8}\text{Ti}_{42.2}\text{Hf}_8$ strips. The strips were chemically and structurally homogenous along their length but not along their width: grains size was bigger on the edges than in the centre, which is inherent to the technique.

In our process the raw material is placed into a VIM furnace, in which the material melts. After melting, the melt is, based on gravitational force and computerized drawing mechanism, moved against the nozzle, which adjusts the rate and direction of the melt flow. Melt flows through the nozzle into a water-chilled mould, where the melt is solidified, and obtains the final rod shape.

Chapter 3

Materials and Methods

3.1 Materials

- Ni tablets (99,8 % purity),
- Ti pellets (99,99 % purity),
- clay graphite crucible,
- Cu mould (99,9 % purity),
- Fe screw (99,8 % purity),
- ZrO_2 nozzle stabilized with Y_2O_3 (> 94 wt.% zirconia, > 5 wt.% yttria, $< 0,3$ wt.% Al_2O_3 , $< 0,02$ wt.% SiO_2 , $< 0,01$ wt.% Fe_2O_3) and
- Vacuum Induction Furnace with mechanism for Continuous Casting at Faculty of Mechanical Engineering, Maribor, Slovenia (Figure 8).



Figure 8: Vacuum Induction Furnace with mechanism for Continuous Casting.

3.2 Continuous Vertical Casting of NiTi Alloy

The continuous casting device in Maribor has 4 main parts: a crucible where the melting temperature is maintained and the melt is directed to the primary cooler, the crystallizer (mould and primary cooler) is a part where liquid to solid phase transformation occurs to the extent that

it does not cause damage to the already hardened zone (skin), the secondary cooler has the task of further solidification of the material and the drawing mechanism represented by the drawing and pressing rollers driven by electronically controlled electric motors. The most important part is the crystallizer. In the crystallizer there are 3 essential regions: liquid (melt), transition (melt + solid) and solid region. In the liquid region, the material's contact with the wall is perfect and the heat transfers with conduction and convection. In the transition region the heat flows are rising, the convection is reducing. The solid region can be divided into 2 parts. In the first part the skin is not yet sufficiently solid, so the pressure pressed it against the wall, which allows good contact with the wall and intense cooling. In the second part, a gap between the wall and the material that is shrinking appears. In the first part heat transfers as conduction, in the other as a radiation and as a conduction through a medium in the gap. The heat flux density therefore begins to fall, so the mould must not be too long and the drawing too slow [71].

The NiTi alloy was obtained with the combination of techniques: Vacuum Induction Melting (VIM) and Continuous Casting (CC). For VIM, a clay-graphite crucible was filled up to 2/3 of its volume due to the high metallo-static pressure (pressure that occurs within a molten metal) with Ti pellets and Ni tablets. The clay graphite crucible consists of graphite with clay as the bonding agent. The clay forms a ceramic bond and the graphite provides thermal and electrical conductivity. The crucible is coated with a glaze that prevents oxidation which is crucial due to the high oxygen affinity of titanium [72]. The induction flux is heating the electrically conductive clay-graphite crucible through which the heat flow is transferred to nickel and titanium that are melting. By melting of nickel and titanium with VIM at a temperature about 1450 °C a pressure lower than 10^{-2} mbar was achieved in the system. The induction power during heating was for first 10 minutes 10 kW, then next 10 minutes 20 kW and in final 5 minutes 30 kW. The temperature heating regime diagram (Figure 9) shows that for the first 3 hours the temperature was constant (20 °C) and within this time the VIM furnace was vacuuming to achieve the pressure below 10^{-2} mbar. Then, in the next 20 minutes the temperature was rising linearly from 20 to 1000 °C. finally, the temperature between 1000 °C and 1450 °C was increasing for 100 °C every 5 minutes in a step mode.

When the NiTi alloy was melted, its drawing into the form of rods started. As seen in Figure 10, the drawing takes place in a copper mould with a diameter of 12 mm, which has a covering made of stainless steel. At the mould entry there is a ZrO₂ nozzle, stabilized with Y₂O₃ and the entire mould is equipped with a cooling system that cools the cast. The temperature of the cooling water that enters the system is 8 °C. This water then circles through the mould system and accepts the heat of the alloy. The water temperature on the exit side is 22 °C. The driving force for moving the melt against the nozzle are gravity and computerized drawing mechanism. The temperature of the alloy in the nozzle, just before the drawing begins, should be equal to the solidification temperature of nitinol. The drawing of the rod was carried out in the sequence of pull-pause, as this reduces the possibility of a reaction between the alloy and the mould, as well as the porosity of the material or the occurrence of cracks in the material [73]. The drawing stroke had a length of between 0 and 10 mm and the pause lasted between 0 and 1 s. The induction power during casting was between 25 and 30 kW. Continuous vertical casting was operating in the mid-range frequency (4 kHz).

The chemical composition of NiTi alloy was measured using Inductively Coupled Plasma Optical Emission Spectroscopy – ICP-OES (Agilent 720, IMT, Ljubljana, Slovenia) and X-ray fluorescence – XRF (Thermo Scientific Niton XL3t GOLDD+, IMT, Ljubljana, Slovenia).

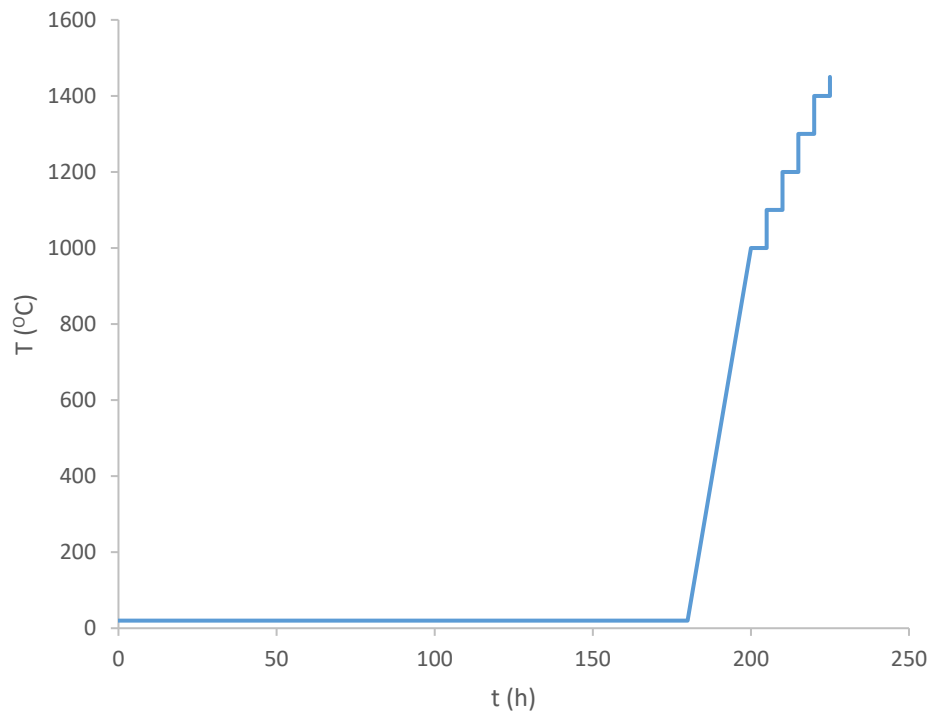


Figure 9: Temperature heating regime by Vacuum induction melting.

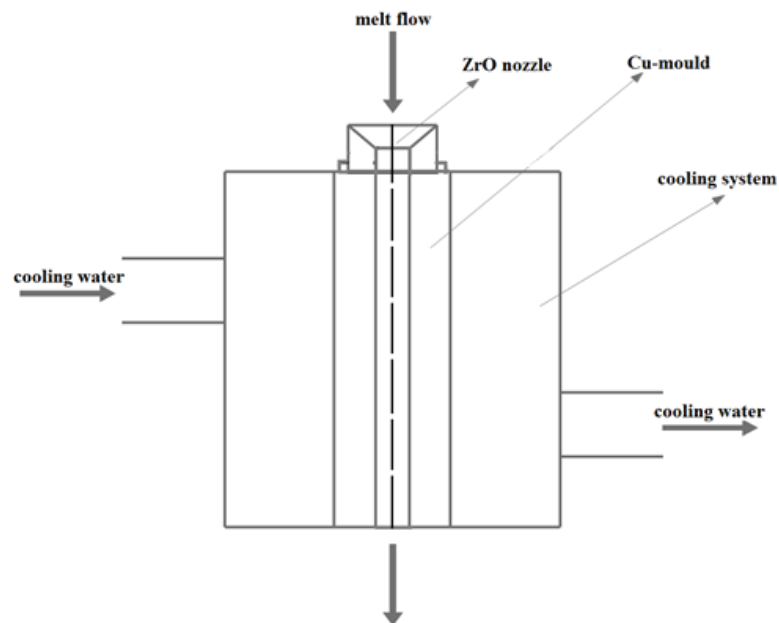


Figure 10: Schematic presentation of copper mould with cooling system.

3.3 Sample Preparation

CVC NiTi rod was cut longitudinally (according to the direction of casting) for microstructure investigation and transversally in the cylinder shape with the diameter of the rod (approximately 11 mm) and a width of 1cm. For this purpose, an Accutom 50 (IMT, Ljubljana, Slovenia) electronic saw was used for precision cutting. Commercial NiTi, which was in the rolled state in

the form of sheets with width of 1.5 mm, was cut to circles with diameter of 10 mm and width of 1.5 mm using water jet cutter. These cut samples of commercial NiTi and CVC NiTi rod were used for investigation of microstructure, deposition of TiO₂ layer using ALD, biocompatibility and corrosion resistance measurements.

For easier polishing, the samples were then hot-pressed into Bakelite. Mechanical polishing was performed on Struers Abramin apparatus (IMT, Ljubljana, Slovenia). The grinding was performed with 320-grit SiC abrasive paper, mechanical polishing with MD-Largo discs with 9 µm diamond suspension and with peroxide grains in a chemically aggressive suspension – OP-S (colloidal silica). At the end samples were cleaned with detergent, well washed with water and put in an ultrasound bath in alcohol. For the microstructure characterization, samples were then etched with Kroll's reagent (3 ml HF, 6 ml HNO₃ and 100 ml of distilled water).

3.4 Microstructure Investigation

A basic microstructure investigation (visibility of crystals and grain boundaries) of CVC NiTi rod was performed using light microscope Microphot FXA (IMT, Ljubljana, Slovenia), where the images are taken by Nikon with 3CCD- Hitachi HV-C20A camera.

Detailed microstructure investigation (visibility of different phases within the grains, presence of inclusions) of CVC NiTi rod was performed using Scanning Electron Microscopy - Thermal Field Emission SEM JEOL JSM-6500F, equipped with Energy-dispersive X-ray spectroscopy (EDS), Wavelength-dispersive X-ray spectroscopy (WDS) and Electron backscatter diffraction (EBSD) analytical techniques (IMT, Ljubljana, Slovenia), shown in Figure 11. Secondary-electron images and backscattered electron images were recorded at different magnifications and SEM working parameters of 15 kV voltage, 7 nA probe current and 10 mm working distance. Energy-Dispersive X-Ray Spectroscopy (EDS) was performed using OXFORD EDS INCA ENERGY 450 with INCA X-SIGHT LN2 type detector (IMT, Ljubljana, Slovenia). With the EDS analysis the composition of individual phases and inclusions was investigated.



Figure 11: Thermal Field Emission SEM JSM-6500F at IMT, Ljubljana, Slovenia.

3.5 Mechanical Properties of CVC NiTi Rod

- Hardness measurement

Hardness is resistance of metal to plastic deformation, usually by indentation [74]. The hardness of the CVC NiTi rod was measured by Vickers. For this purpose, the CVC NiTi rod was cut transversally. Vickers hardness was measured in multiple points from the end of the rod to the center (radius) of the rod. Vickers hardness was performed on Instron Tukon 2100B (IMT, Ljubljana, Slovenia), shown in Figure 12. The selected load was HV0.1, which means that a force of 0.98 N was used.



Figure 12: Instron Tukon 2100B for Vickers hardness measurement at IMT, Ljubljana, Slovenia.

- Tensile and compressive test

With tensile and compressive test elasticity and tensile strength of CVC NiTi rod was determined. Both tests were accomplished at room temperature (20 ± 0.5 °C). Tests were performed on INSTRON 1255, 500 kN device (IMT, Ljubljana, Slovenia), shown in Figure 13. Preload force was 1kN and the velocity of deformation increase was 0.00025 s^{-1} in tension and in compression the preload force was 1kN and the compression velocity was 2 mm/min.



Figure 13: INSTRON 1255, 500 kN device for mechanical tests at IMT, Ljubljana, Slovenia.

The tensile test samples were turned according to the B8 $\times$ 40 standard (Figure 14a). The diameter of the specimens was 8 mm, and their length was 40 mm, and an M10 thread was used. The compressive test samples were turned into cylinders with a diameter of 10 mm and a height of 12 mm (Figure 14b).

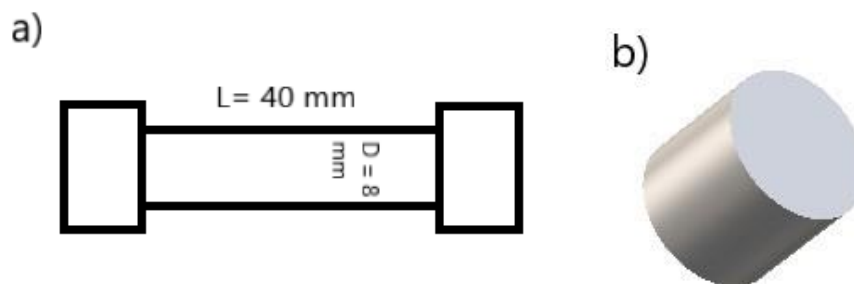


Figure 14: a sample for a) tensile test and b) compressive test.

- 4-point bending test

Bending characterizes the behaviour of a specimen subjected to an external load applied perpendicularly to a longitudinal axis of the specimen. The 4-point bending test has, in addition

to two supporting pins, also two loading pins that transmit force to the test specimen [75-77]. The 4-point bending test was accomplished at room temperature (19 °C). Tests were performed on AMSLER device (IMT, Ljubljana, Slovenia). The preload force was 0.0125 kN and bending velocity was 0.5 mm/min. The 4-point bending test specimens were turned into cylinders with diameter of 4 mm and length of 12 mm (Figure 15).

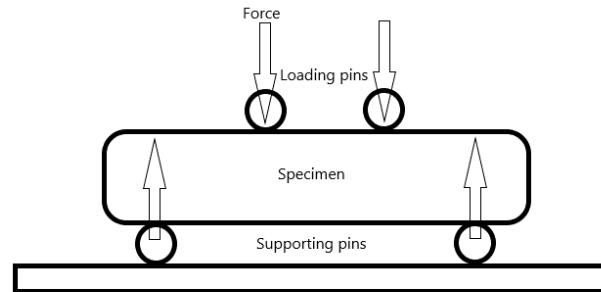


Figure 15: A sample for 4-point bending test.

3.6 Atomic Layer Deposition of TiO₂ Layer

Atomic layer deposition (ALD) is an interesting technique for producing TiO₂ thin films due to its simplicity, reproducibility, the high conformity of thin films and an excellent control of the layer thickness at the angstrom level. The thin film is formed as a result of repeated deposition cycles. At least two subsequent self-limited surface reactions are used to form a new layer [78-81].

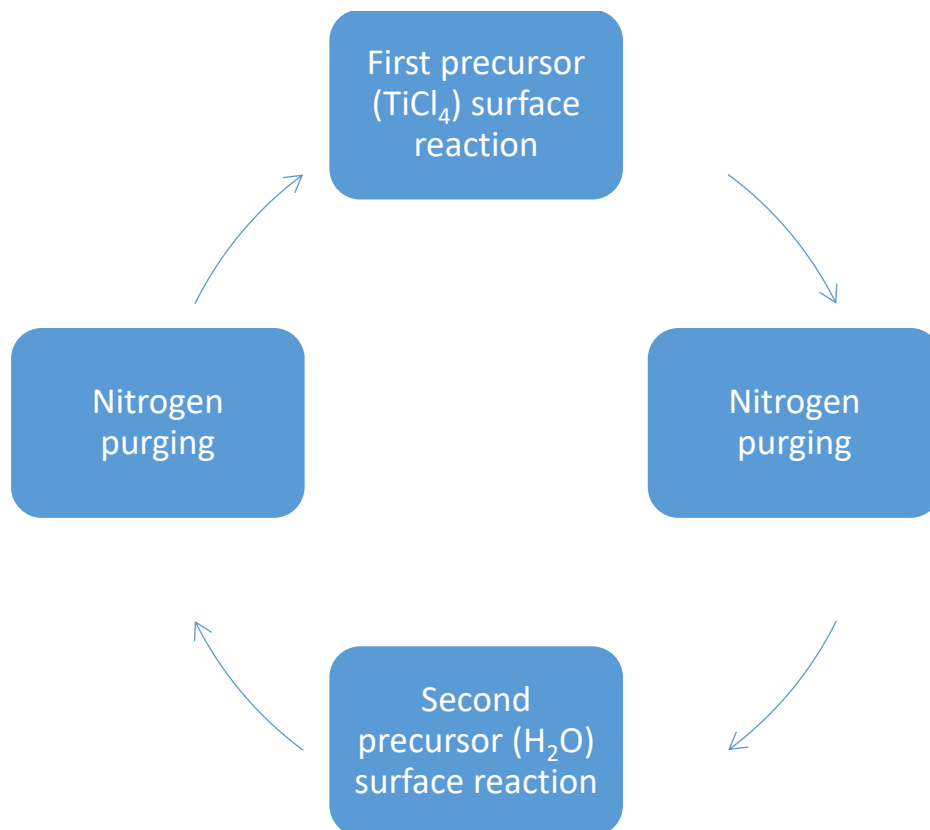
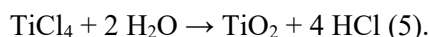


Figure 16: Steps by ALD deposition.

The process of depositing the layer onto the surface with ALD is cyclic. Each cycle is set up from 4 steps (Figure 16). In the first step, the first precursor (TiCl_4) is pulsed into the reactor. TiCl_4 is adsorbed to the sample's surface and reacts there with reactive sites (initially these are organic impurities). In the second step nitrogen is pulsed into reactor to purge the excess of the reactant and by-products. In the third step, the second precursor (H_2O) is pulsed into the reactor. H_2O is adsorbed to the samples surface and reacts there with reactive sites. In the last step, nitrogen is again pulsed into reactor to purge the excess of the reactant and by-products. The simplified equation for this reaction is:



The deposition of TiO_2 layer on the surface of CVC NiTi rod and commercial NiTi was accomplished in a Beneq TFS 200 system (Figure 17) at 250°C . The pulsing times for TiCl_4 and H_2O were 250 ms and 180 ms, followed by appropriate purge cycles with nitrogen (3 s after TiCl_4 and 2 s after H_2O pulses).



Figure 17: Beneq TFS 200 system for Atomic Layer Deposition at University of Rijeka, Croatia

To confirm the formation of TiO_2 layer, the XPS spectra were recorded with a SPECS spectrometer equipped with the Phoibos MCD 100 electron analyser and a monochromated source of Al $\text{K}\alpha$ x-rays of 1486.74 eV.

3.7 Biocompatibility

Human Umbilical Vein Endothelial Cells (HUVEC cells) were cultured in Dulbecco's modified Eagle's medium, in which 4-mM L-glutamine and 10 % (v/v) foetal bovine serum (FBS) was added. Cells were grown at 37°C in a humidified atmosphere with 5 % CO_2 and were routinely passaged twice a week. Prior to experimental work, cells were confirmed to be mycoplasma negative using the MycoAlertTM Kit (Biotechnical Faculty – Department of Biology, Ljubljana, Slovenia).

Biocompatibility tests were performed on CVC NiTi rod, CVC NiTi rod with 50 nm TiO_2 layer, commercial NiTi and commercial NiTi with 50 nm TiO_2 layer samples. All samples were UV sterilised before performing cell experiments. Sterile samples were aseptically put into the 12-well plates and then the cells were seeded into each well (2×10^4 cells/cm²). After a 24-hour incubation, allowing the cells to adhere, the cells on the samples were rinsed with Dulbecco's Phosphate-Buffered Saline (to remove any floating, unattached cells) and stained with 2 $\mu\text{g/mL}$ Hoechst 33342 and 2 $\mu\text{g/mL}$ Propidium iodide for 20 min. Hoechst 33342 stains nuclei of all cells

blue, while Propidium iodide stains nuclei of dead cells red. Stained cells that were adhered to the samples were observed with a fluorescent microscope Axio Imager.Z1 (Biotechnical Faculty – Department of Biology, Ljubljana, Slovenia) immediately after the staining. For each sample, several representative pictures at 25 $\times$ and 100 $\times$ magnifications were taken. The pictures were processed by the use of ImageJ 1.46 r software, where the number of all attached cells (based on the number of blue nuclei) and the number of dead cells (based on the number of red nuclei) were evaluated.

After microscopic observation, samples with attached cells were inserted into the Karnovsky fixative, consisting of 2.5 % glutaraldehyde and 0.4 % paraformaldehyde in 1-M Na-phosphate buffer ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$). After 3h incubation at room temperature, fixative was removed and samples were washed for 3×10 min with 1-M Na-phosphate buffer. The post-fixation of samples was accomplished by 1% osmium tetroxide (OsO_4) for 60 min, followed by washing in distilled H_2O (3×10 min). Samples were dehydrated with 30 % ethanol for 10 min, 50 % ethanol for 10min, 70 % ethanol for 10min, 80% ethanol for 10 min, 90% ethanol for 10 min and absolute ethanol for 10 min. Further dehydration steps were performed with a mixture of Hexamethyldisiloxane (HMDS) and absolute ethanol (1:2, v/v, 10 min; 1:1, v/v, 10 min) and with absolute HMDS (10 min), which was left to evaporate for 24 h.

After the cells were fixed, images of cells on the surface of the samples were recorded with light microscopy Microphot FXA (IMT, Ljubljana, Slovenia), where the images were taken by Nikon with 3CCD- Hitachi HV-C20A camera. The proportion of the occupied surface with cells was measured using optical microscopic images and the computer software analySIS.

3.8 Corrosion Tests

Corrosion tests were performed on CVC NiTi rod, CVC NiTi rod with 50-nm TiO_2 layer, commercial NiTi and commercial NiTi with 50 nm TiO_2 layer samples. All the measurements were held at body temperature (37 $^\circ\text{C}$). Potentiodynamic polarisation measurements and electrochemical impedance spectrometry (EIS) have been used to study the electrochemical behaviour of samples. All the measurements were recorded by BioLogic Modular Research Grade Potentiostat/Galvanostat/FRA Model SP-300 with an EC-Lab Software and three electrode cell (IMT, Ljubljana, Slovenia). In this cell, the sample was a working electrode, saturated calomel electrode (SCE, 0,242 V vs. SHE) was used as a reference electrode and the counter electrode (CE) was a platinum net. The experiment was held in simulated physiological Hank's solution, containing 8 g/L NaCl, 0.40 g/L KCl, 0.35 g/L NaHCO_3 , 0.25 g/L $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 0.06 g/L $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, 0.19 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.41 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.06 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 1 g/L glucose, at pH = 7.8. All the chemicals were from Merck, Darmstadt, Germany. The potentiodynamic curves were recorded after 1 hour sample stabilisation at the open-circuit potential (OCP), starting the measurement at 250 mV vs. SCE more negative than the OCP. The potential was then increased, using a scan rate of 1 mV s^{-1} , until the transpassive region was reached. Long-term open-circuit potentiostatic electrochemical impedance spectra were obtained for the investigated samples. The impedance was measured at the OCP, with sinus amplitude of 5 mV peak-to-peak and a frequency range of 65 kHz to 1 mHz, in the sequence of 0h, 1h, 2 h, 6 h, 12 h, 24 h, 48 h, 72 h, 96 h, 120 h, 144 h, 168 h and 192 h. The impedance data are presented in terms of Nyquist plots. For the fitting process Zview v3.4d Scribner Associates software was used.

Chapter 4

Results and Discussion

4.1 VIM Batch Casting of NiTi Alloy

First, we tested the melting of NiTi alloy in a vacuum induction furnace with which we wanted to determine how the melting path and how the chemical composition changes depending on the melting parameters (temperature, pressure, heating regime, crucible and mould material, cooling, etc.). A clay-graphite crucible was selected for the melting experiments. The amount of nickel and titanium (total of 15 kg) was determined according to the size of the crucible (Figure 18a), since it was necessary to ensure that it was filled up to $\frac{1}{2}$. This condition was demanded by induction melting for the melting process to start, as well as to ensure sufficient metallo-static pressure required during subsequent continuous casting. In carrying out the experiment, it was necessary to appropriately place metals in a clay-graphite crucible (sequence) in order to mix the two components during melting, since there is a large difference in the viscosity between the two metals, while the reactivity of Ti with O is significantly higher compared to Ni. During the experiments, it was therefore necessary to maintain an appropriate vacuum and vacuuming regime with Ar 5.0.

Considering that Ni melts at a temperature 200 °C lower than Ti, so the diffusion of C in the molten Ni is faster than in the solid Ti. From this point of view, the walls of the graphite crucible need to be coated with Ti. But on the other hand, molten Ti has a high viscosity which makes it difficult to mix in the crucible. From this perspective, it is necessary to give Ti on the location of a more intense mixing (centre of the crucible). Thus, Zhang Z. et al. [82] and Frenzel J. et al. [2] suggested a compromise in which the crucible walls are stored with a layer of Ti pellets. Those pellets prevent direct contact of Ni with C, and then the crucible is filled up with Ni and Ti in the middle of the crucible (Figure 18b). Another problem is accurate measurement and regulation of the temperature, which was very difficult because the thermocouple was not in constant contact with the melt due to the potential contamination of the melt and the temperature at the crucible wall is quite different from the actual temperature of the melt. The frequency of induction is also very important for the casting, as a high frequency enables the temperature to rise and low frequency means more intensive stirring. In this case the casting was operated at a mid-range frequency of induction (4 kHz) that does not provide adequate mixing power causing undesirable chemical composition in some places of the rod. Another difficulty is high titanium reactivity with almost all elements. There are some materials, like crucible, nozzle and starter bar, that are in contact with the NiTi melt, which increases the possibility of the reaction with titanium. A clay-graphite crucible is coated with a glaze that is sufficient enough to suppress the diffusion of carbon into the NiTi melt.



Figure 18: a) Clay-graphite crucible and b) the correct sequence of filling up from the walls to the middle of the crucible: Ti-Ni-Ti.

The alloy was poured into a steel mould ($p = 10^{-2}$ mbar and $T = 1380$ °C) and allowed to cool at room temperature. We took a sample for the ICP analysis from the casting. The ICP chemical analysis showed the desired NiTi alloy composition (50 at.% Ni and 50 at.% Ti). From the optical and secondary electron images (Figure 19), it is evident that the NiTi alloy obtained this way has the dendritic microstructure, which consists of the primary dendrites and the interdendritic space (the bright, smaller area in Figure 18a, or the dark area in Figure 18b). Grains do not have a uniform orientation, their growth was in the opposite direction of the heat dissipation in the mould.

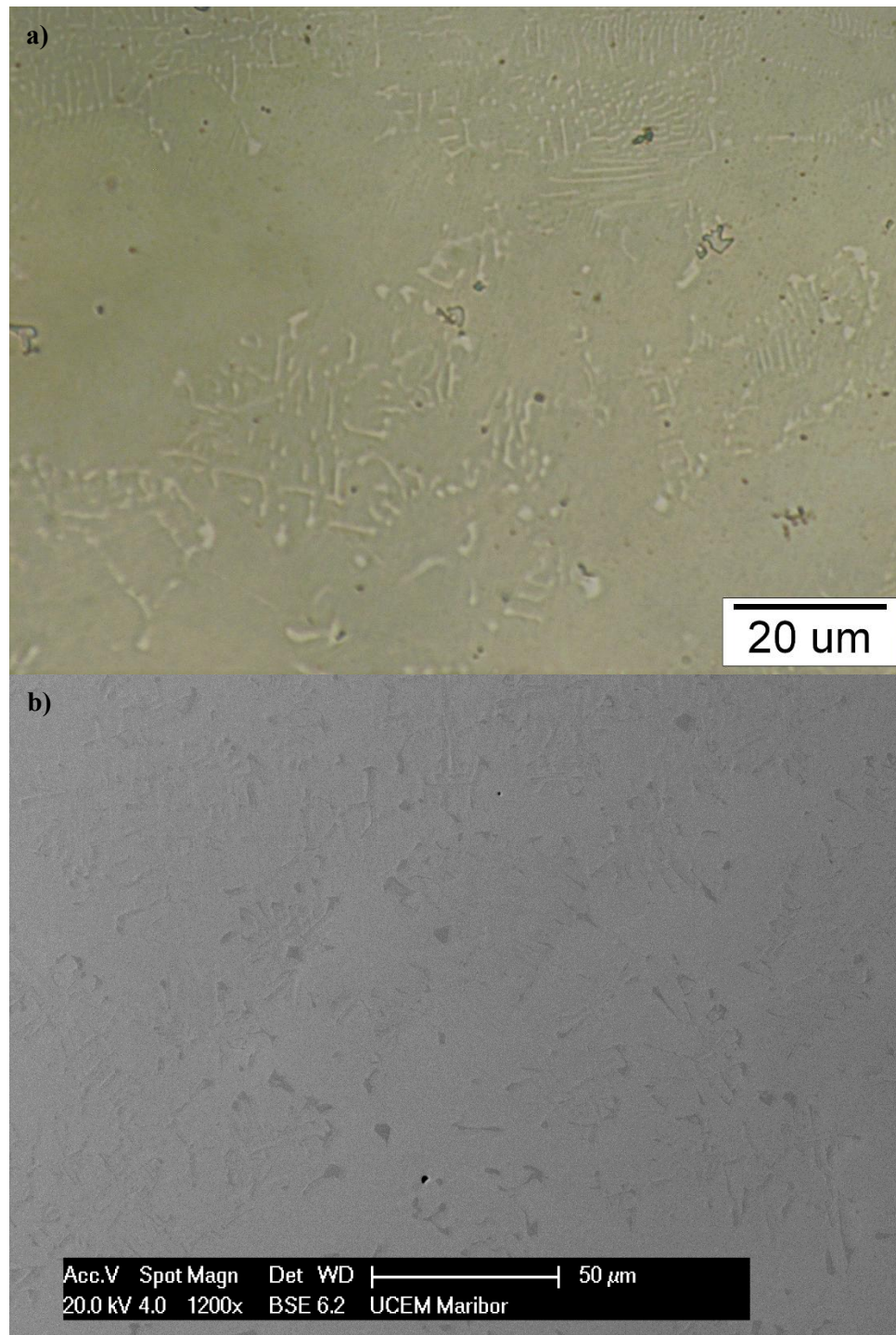


Figure 19: a) Optical microscope image at 1000-x magnification and b) SE image at 1200-x magnification of NiTi alloy, produced by batch casting.

4.2 Continuous Vertical Casting of NiTi Alloy and its Microstructure

Based on the knowledge of the NiTi alloy melting technique we proceeded to continuous casting. The advantage of continuous casting is that the melt flows through the shortest path to the solidification site, whereby the casting shape does not change and ensures the continuity of the process. The continuous casting is a process with a constant feeding of alloy into the furnace, and constant drawing of the alloy at the end of the process. In contrast to the classic casting considerably smaller semi-finished products are made, which can be then further processed more

easily. In our case of the continuous vertical casting experiment, the direction of gravity and flow of the molten alloy or rod was uniform during the solidification.

CVC of NiTi alloy is a complex process that requires precise process parameters, which are connected to 4 systems: casting part, crystallizer, secondary cooling system and drawing mechanism. The most demanding part is the crystallizer, together with the nozzle, as it is the basis for the continuity of the casting procedure. On the basis of previous studies, we determined the appropriate construction and material of the nozzle to be ZrO_2 . In the drawing mechanism, it was necessary to determine the appropriate drawing starter bar and the optimal drawing rate, which is usually not constant, but it is changing so we are talking about i.e. step mode. We confirmed that Fe starter bar is not the optimum possible option, since the NiTi rod contained app. 1 at.% of Fe. Also, we have confirmed the reaction between zirconia nozzle and NiTi melt. We made an experiment where we gave a zirconia stick into the NiTi melt at 1450°C and after some time we took the stick out of the melt and we observed that zirconia stick was consuming during its exposure with the NiTi melt. The reaction occurred, although in theory the Gibbs free energy for reaction between ZrO_2 and Ti is negative at high temperatures [83]. In further experiments the Fe starter bar and zirconia nozzle will be replaced with Ti starter bar. The drawing rate of the rod is also an important factor. When the drawing is too slow, the temperature decreases, which leads to solidification of the alloy in the nozzle and retraction of further drawing. This leads to fracture of the rod and the process ends without the desired result. The rod also breaks when the drawing rate is too fast due to the adhesion to the mould and the weakness of the thin solidified shell [73]. We performed series of CVC experiments using different process and drawing parameters. One example is in Table 1. With first attempt a 3 m long rod with diameter of approximately 11 mm was obtained (Figure 20). The rod was shiny, silver coloured with visible periodic marks on its surface.

Table 1: Example of parameters used by CVC experiment.

Diameter of the rod	12 mm
Alloy	nitinol
weight/m	ca. 700 g/m
Step	8 mm
Waiting time 1	0,5 s
Motor velocity	20 %
Casting velocity	cca. 600mm/min
K motor	23,5
K rod	42
Mould cooling	max.; ca. 26 l/min
Crucible	Clay graphite
mould	copper
nozzle	ZrO_2
Melting temperature	1450°C
Rod length	55 cm

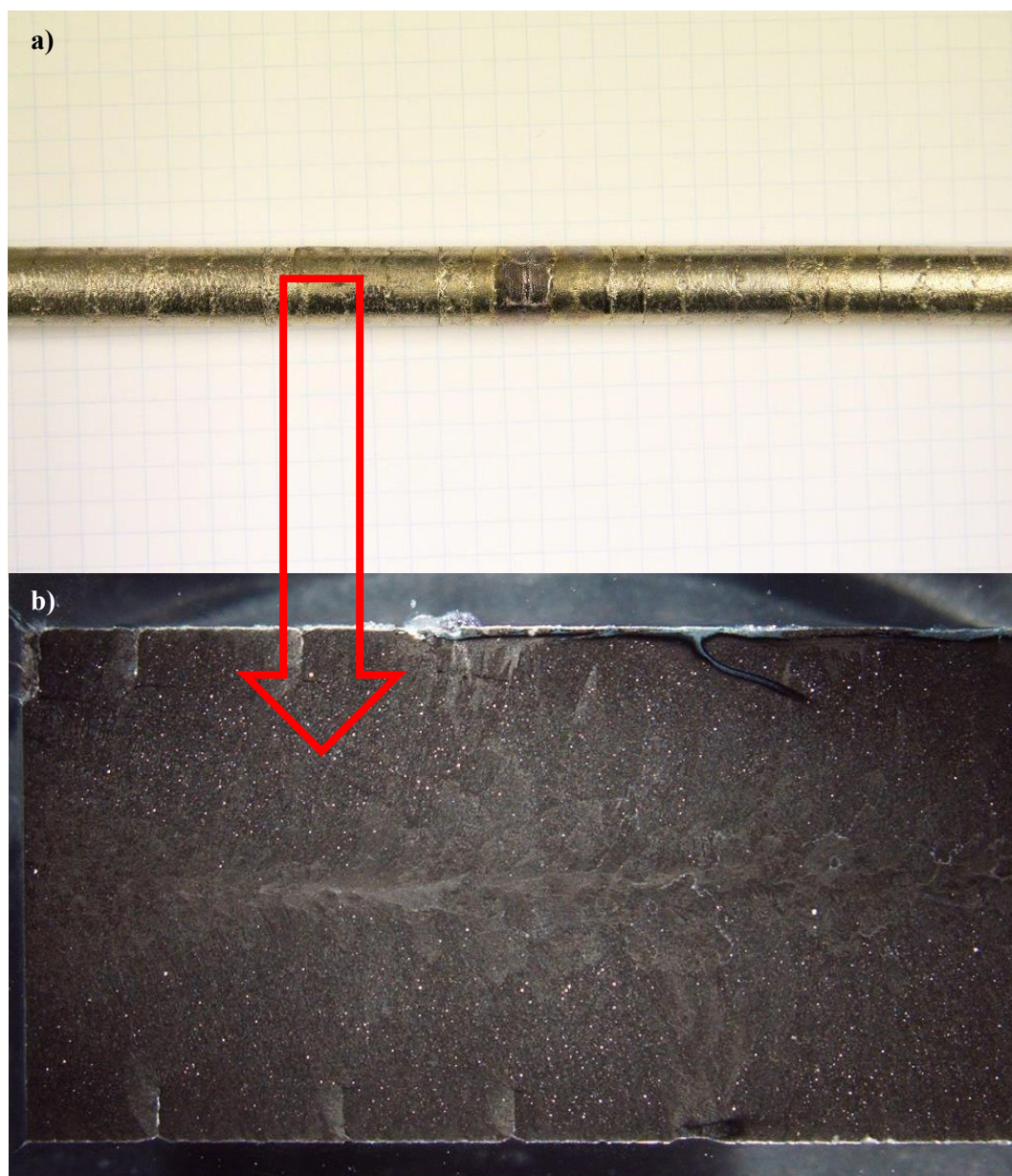


Figure 20: a) CVC NiTi rod and b) longitudinally macroscopic image of CVC NiTi rod.

ICP analysis for the first attempt of CVC NiTi rod showed a constant material composition of 59.8 at.% Ni, 38.9 at.% Ti and 0.3 at.% C, EDS analysis showed approximately 1 at.% Fe. Deviation from the desired value (50 at.% Ni) is probably caused by complications with stirring of the melt (better mixing takes place at a lower frequency induction, Ti is very difficult to mix, measurement error). The source of Fe could be attributed to the Fe screw which was used as starter bar. During further experiments we obtained only 10–15-cm-long rods. Their chemical composition varied during casting. At the beginning of drawing XRF analysis showed that the rods were rich with nickel (app. 70 at.% Ni; app. 27 at.% Ti) and with the increasing length of the rods nickel content decreased. Chemical composition at rods fracture was app. 52 at.% Ni and app. 47 at.% Ti, which is very close to the desired chemical composition. . The difference in concentration between the two sides of the NiTi rods can be attributed to poor stirring of the NiTi melt, while fast collapse of the rod is a result of too fast or too slow drawing rate and the reaction between zirconia nozzle and titanium from the NiTi melt that causes the deposition of titanium oxide on the nozzle which eventually clogs the nozzle and prevents further drawing of NiTi rod. All further investigations were performed only on the rod of the first CVC experiment, and will be simply called the CVC NiTi rod.

4.2.1 Microstructure of CVC NiTi Rod

Jiang S et al. [84,85] reported that microstructure of as-cast NiTi alloy after water-cooled casting is dendritic and the grains are equiaxed and very inhomogeneous. The microstructure of our NiTi rod is in the longitudinal direction dendritic, with a radial orientation of the grains. The microstructure changes along the rod radius, and from a distance from the shell of a rod, it passes from fine-grained to rough with heavily expanded dendritic branches and a greater proportion of the interdendritic eutectic. In the microstructure there are no visible defects such as cracks and other type of porosity.

The matrix phase of the as-cast NiTi alloy is NiTi and the Ti_2Ni phase is distributed among the matrix phases. The optical microscopy of CVC NiTi rod cross-section reveals the expected dendritic microstructure (Figure 21), where inside the primary phase NiTi is located. This is according to the Ni-Ti phase diagram, where the first solidified phase is NiTi. Dendrites grew in the direction from the coldest location (from the walls of the nozzle) to the middle of the rod. The orientation of dendrites is random. These dendrites are arranged in the matrix of eutectic (composed with NiTi eut + TiNi_{3-x}). In the microstructure there are no visible defects such as cracks and porosity.

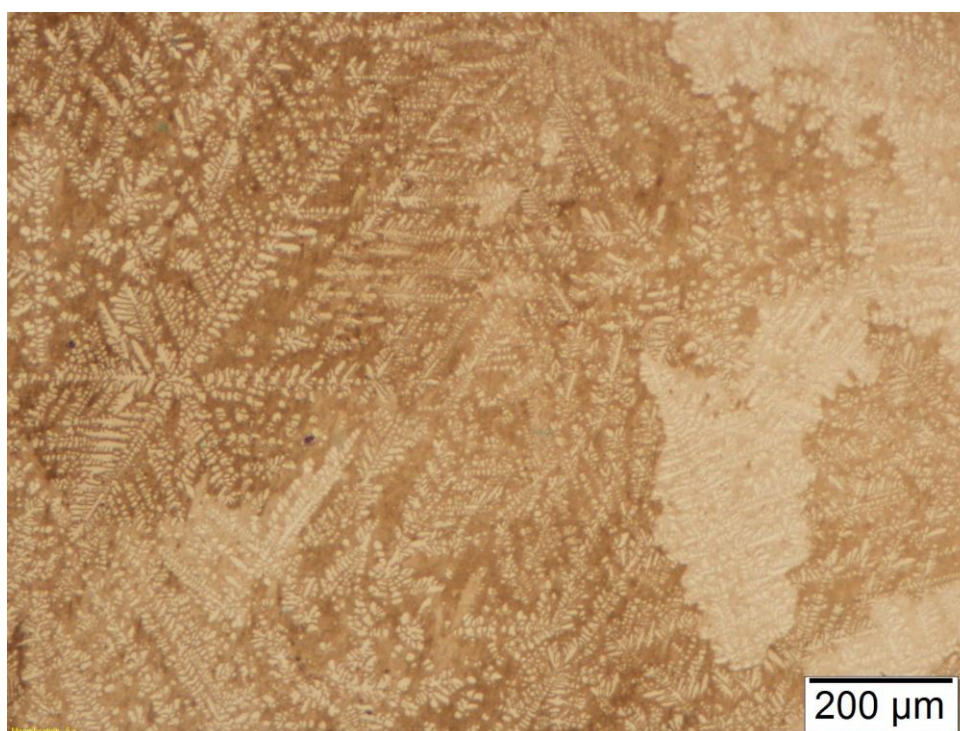


Figure 21: Optical microscope image of CVC NiTi rod at 50 $\times$ magnification.

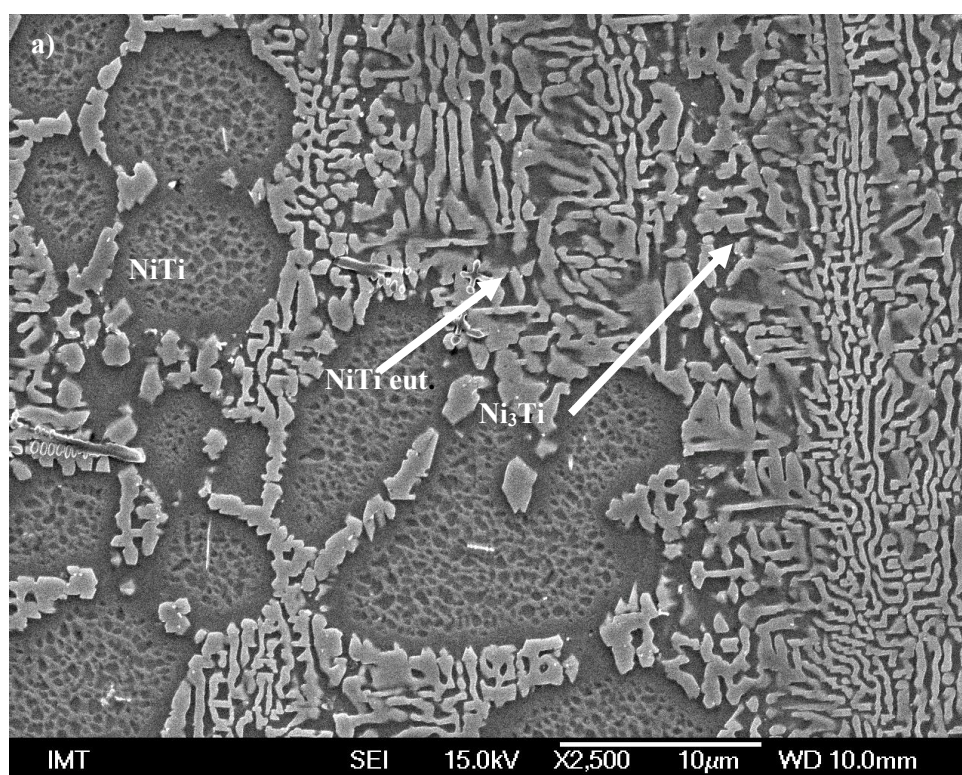
CVC NiTi rod contains approximately 60 at.% Ni. From the Ni-Ti phase diagram (Figure 1) it is clear that this is a hypo-eutectic alloy (according to the eutectic reaction at 1118 $^{\circ}\text{C}$: $\text{L} \rightarrow \text{NiTi} + \text{TiNi}_3$). By an equilibrium cooling the melt would begin to solidify in the temperature range between 1310 and 1118 $^{\circ}\text{C}$. From the melt firstly the primary NiTi phase would solidify that would be continuously generated and grew until the eutectic temperature (1118 $^{\circ}\text{C}$) would be reached. At this temperature, the remaining melt would solidify into eutectic structure composed of a NiTi eut. phase and TiNi_3 phase in the form of lamellas.

In the real case, the cooling is non-equilibrium. Solidifying rates are large, but the diffusion rates in a solid state are too small to make it possible to achieve a homogeneous solid phase. Luo S.B. et al. [32] investigated microstructural evolution of rapid solidified NiTi alloys. They used high Ni content NiTi alloys in the $(\text{Ni}+\text{Ni}_3\text{Ti})$ eutectic range, where the composition of eutectic point is 14 wt% Ti and the eutectic temperature is 1577 K. They observed that a hypoeutectic microstructure is consisting of primary (Ni) dendrites plus interdendritic $(\text{Ni}+\text{Ni}_3\text{Ti})$ eutectic. This microstructural evolution can be transformed to our case but at different eutectic $(\text{NiTi}+\text{Ni}_3\text{Ti})$. Secondary and backscattered electrons image (Figure 22) shows typical dendritic structure (tree-like form) that is solidified primarily (NiTi phase). At the eutectic temperature (1118 $^{\circ}\text{C}$) typical

lamellar eutectic structure ($\text{NiTi} + \text{TiNi}_{3-x}$) is solidified from the residue of the melt. Although there are many researches made with slightly Ni-rich NiTi alloys, only few report about identifying TiNi_3 phase [86] as a consequence of rapid cooling.

EDS analysis at 5 keV voltage (Figure 23 a, Table 2) showed that both the dendritic phase and the dark lamellas of eutectic have a composition of approximately 50 at.% Ni and 50 at.% Ti, while the bright lamellas of eutectic have a composition of 33 at.% Ti and 67 at.% Ni. On the other hand, the EBSD analysis (Figure 23 b) showed that the solidification occurs in accordance with the Ni-Ti phase diagram. The dendrites are 50Ni50Ti, while the lamellar eutectic consist of 2 phases: 50Ni50Ti eut. and Ni_3Ti .

The secondary electrons (SE) image (Figure 24) reveals in addition to the dendritic structure also the presence of the individual inclusions. EDS analysis showed that the inclusions are titanium carbide (TiC). Carbon originates from the clay-graphite crucible and diffuses in the melt during the melting and reacts there with titanium. The Gibbs free energy for formation of TiC is very low, so the conditions for formation of TiC are very favourable. From the results of the EDS analysis it appears that the carbon is located only in the form of carbides, and there is none in the other phases. Ni and Fe are located in the dendrites and the matrix, but not in the carbides, while titanium is present in all the phases. Pan G. et al. [87] reported that when the NiTi alloy contains oxygen, Ti-Ni-O phase precipitates on Ni-Ti grain boundaries. Analysis showed that during CVC, there was no contamination with oxygen because no dissolved oxygen or oxides were observed in the rod. In this manner it could be concluded that the vacuum was appropriate.



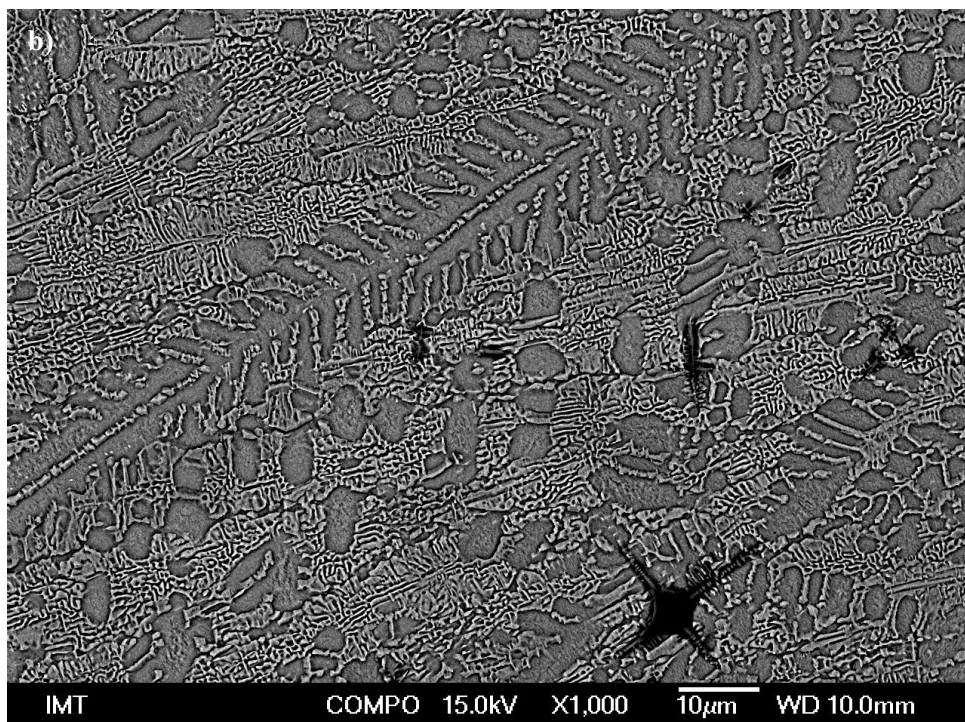
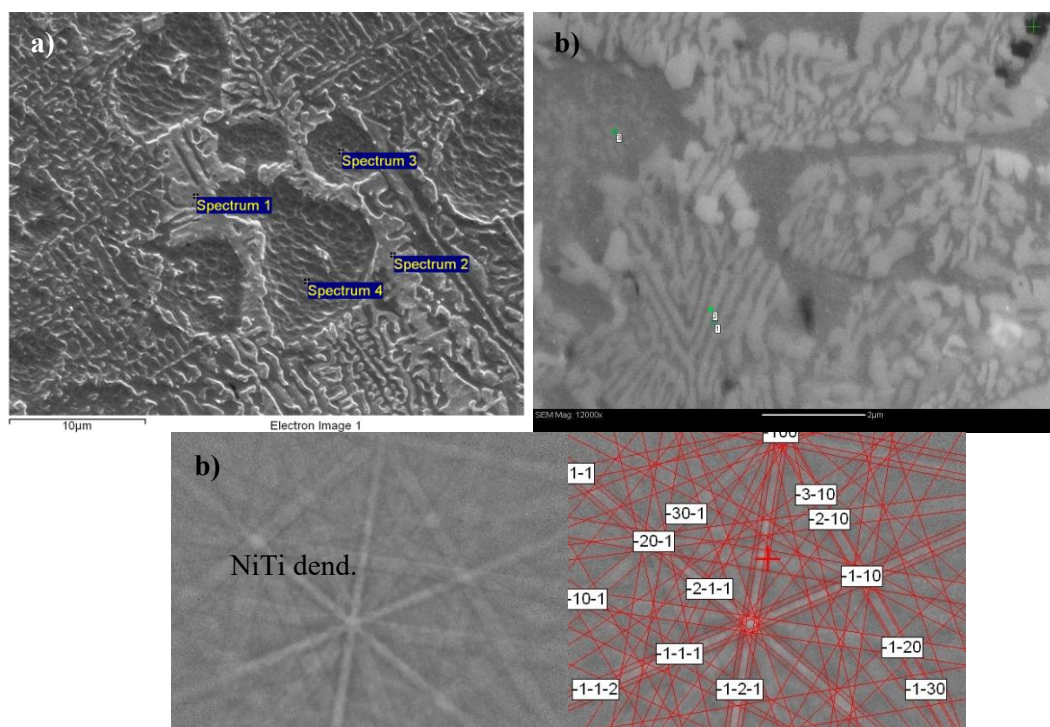


Figure 22: a) Secondary electron image at 2500x magnification and b) backscattered electron image at 1000x magnification of CVC NiTi rod.



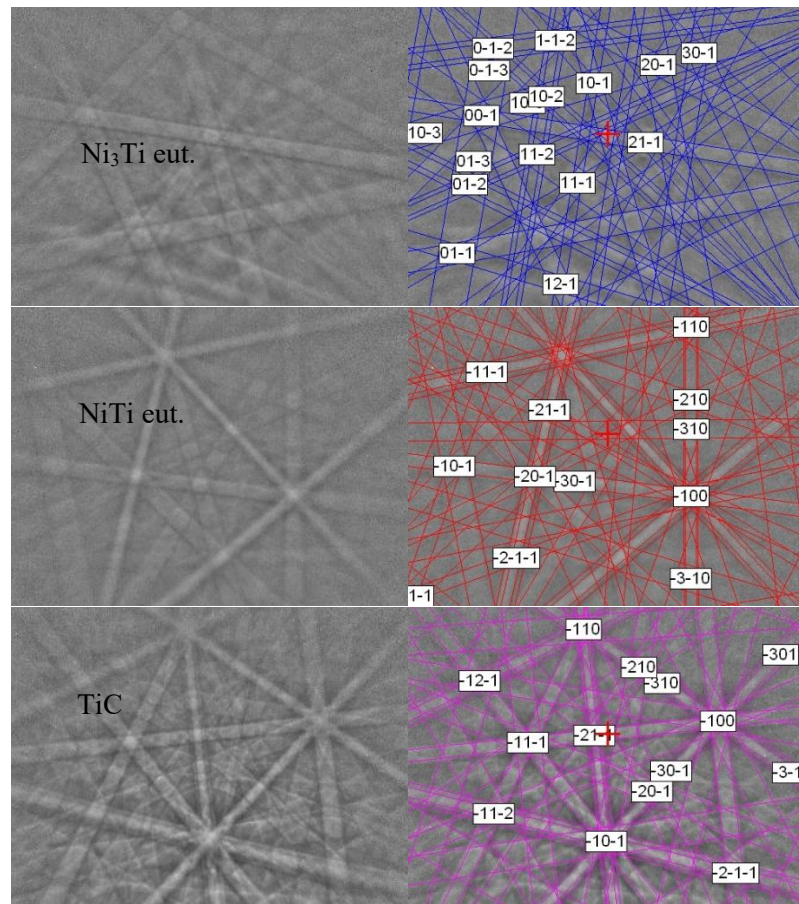


Figure 23: a) Points where EDS analysis was made and b) EBSD analysis of CVC NiTi rod.

Table 2: Results of EDS analysis.

	at.% Ti	at.% Ni
Spectrum 1	36,3	63,7
Spectrum 2	38,8	61,2
Spectrum 3	52,3	47,7
Spectrum 4	55,1	44,9

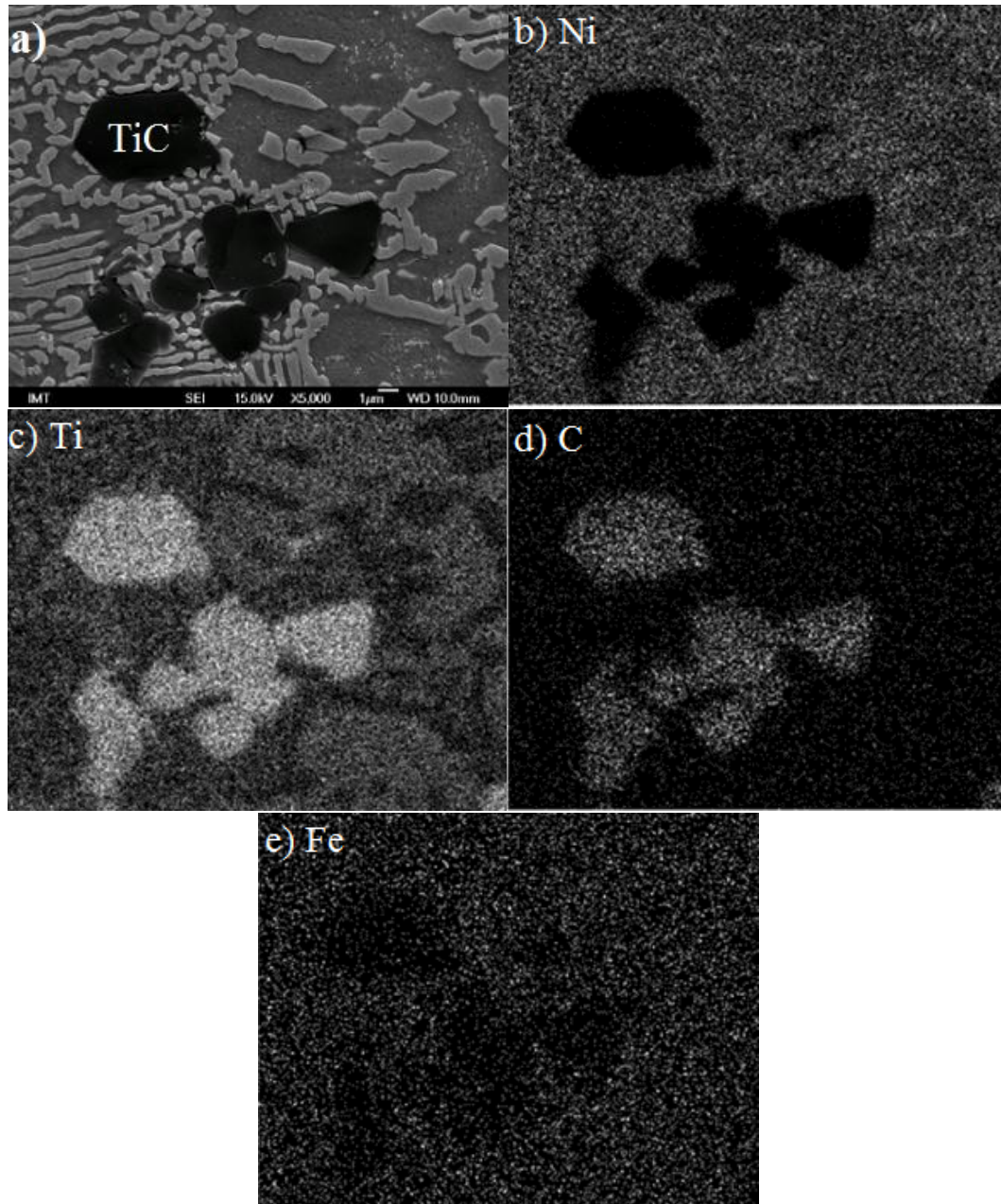


Figure 24: a) SE image of CVC NiTi rod at 5000 $\times$ magnification of area where the TiC inclusions are present, b), c), d) and e) Elemental mapping at the microstructural level by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS) in the area with TiC inclusions.

4.2.2 Microstructure of Commercially Available NiTi Alloy

Further, we compared the microstructure of commercially available nitinol sheet with the as-cast CVC NiTi rod. The optical microscope image of the nitinol's cross-section (Figure 25a) reveals a relatively microstructure that is characteristic for materials that were produced by different forming processes (rolling etc.), since it is possible to notice a characteristic texture. Grains are almost the same size (about 20 μ m), grain boundaries are clearly noticeable. In this case, there is no typical orientation than in the case of the CVC NiTi rod. It is also clearly seen that the alloy contains two different phases: primary (NiTi) + eutectic.

The secondary-electrons image made with SEM (Figure 25 b) reveals that commercially available NiTi alloy consist of 2 phases. The EDS analysis showed that the prevailing phase is

NiTi, containing 50 at.% Ni and 50 at.% Ti. The second phase is carbon rich phase (33.3 at.% C, 40.12 at.% Ti, 26.59 at.% Ni).

Figure 26 shows the distribution of elements in the individual phases of commercially available NiTi alloy.

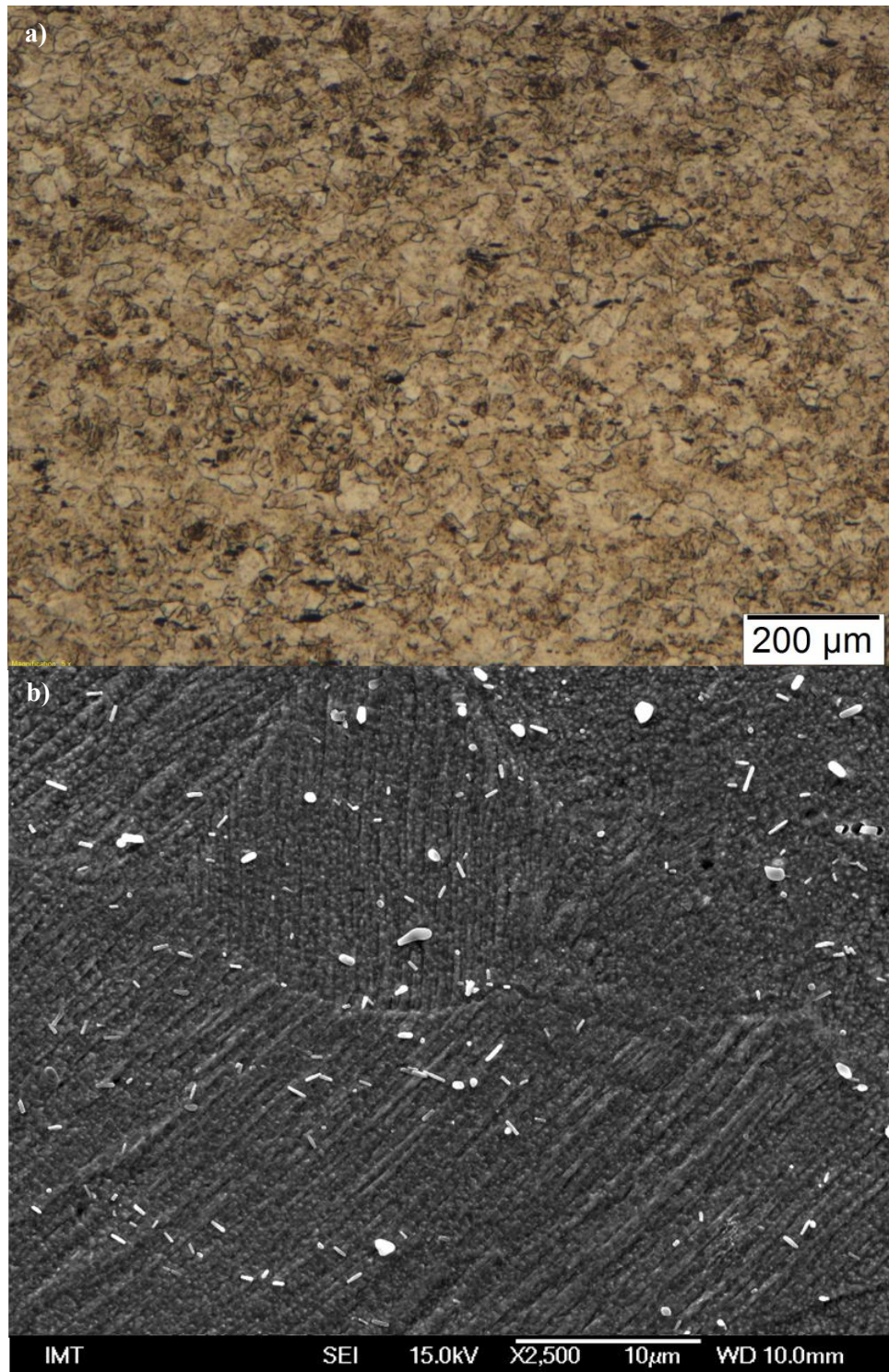


Figure 25: a) Optical microscope image at 50 $\times$ magnification and b) SE image at 2500 $\times$ magnification of commercially available NiTi alloy.

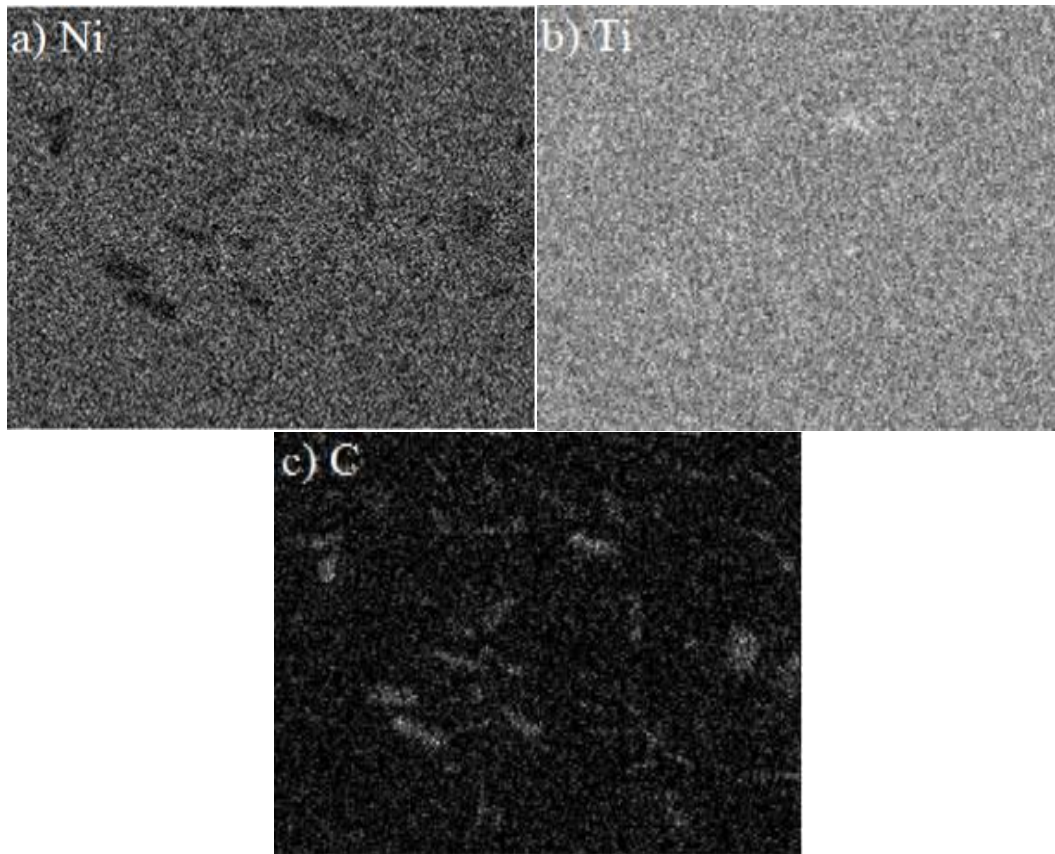


Figure 26: a), b) and c) Elemental mapping at the microstructural level by scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS) of commercial NiTi alloy.

4.3 Mechanical Properties of As-Cast CVC NiTi Rod

For better understanding on how CVC NiTi rod would respond when it would be subjected to some stress, basic mechanical tests, such as Vickers hardness, tensile and compressive test and 4-point bending test, were performed. All the tests were performed on at least two test specimens of CVC NiTi rod, which will be from now on simply called test 1, test 2, etc.

4.3.1 Vickers Hardness

The most basic mechanical test is the measurement of hardness. We measured the hardness of CVC NiTi rod with HV 0,1 pyramid tip, where 0.1 indicates the load used in kgf (kilogram-force). This force was used to make an indentation in our CVC NiTi rod and from the size of the indentation cavity we could assume the hardness of CVC NiTi rod. The measured hardness also depends on the size of the indentation tip. When the tip is small (also its force is smaller), the indentation cavity made with this tip is narrow and shallow, and when the tip is large (and its force is larger), the indentation cavity is wider and deeper. This all indicates that with small tip a smaller area hardness is measured and with large tip bigger area hardness is measured. With small tip enough, we can measure the hardness of a single grain, while with large tips we measure average hardness of more grains, hence the difference in measured hardness [88].

The cooling of CVC NiTi rod during drawing was held perpendicular to the drawing direction. The lowest temperature was on the mould walls or in the edge of CVC NiTi rod and was rising from circumference of CVC NiTi rod to the middle of CVC NiTi rod. In this manner we were interested in how the difference in the cooling temperature between the edge and the middle of CVC NiTi rod affects the hardness of the CVC NiTi rod. The hardness was measured in the CVC NiTi rod cross-section in its radius (from the edge of CVC NiTi rod to the middle of CVC NiTi rod), as shown in Figure 27.

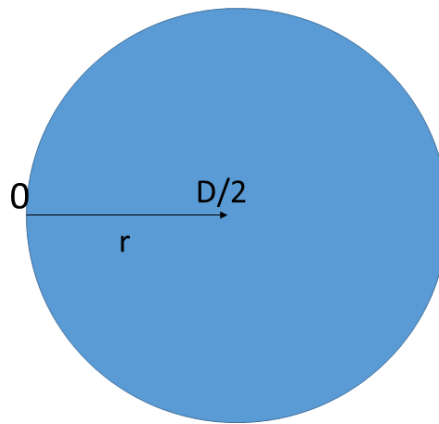


Figure 27: Cross-section of CVC NiTi rod. Hardness was measured in the direction of r : from the edge of the rod (0) to the middle of the rod ($D/2$).

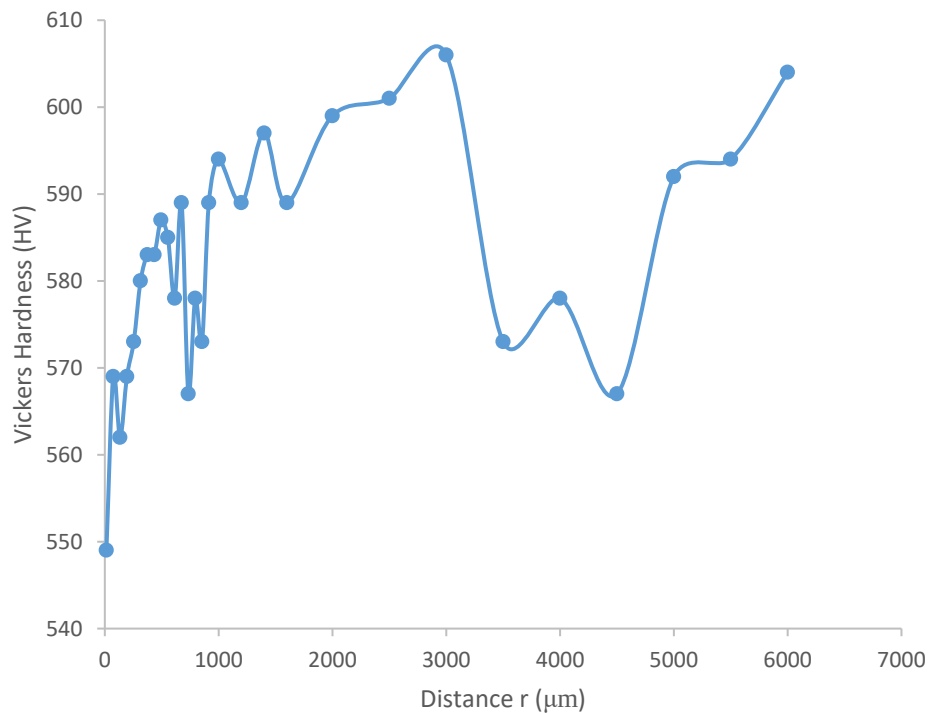


Figure 28: Diagram of Vickers hardness for CVC NiTi rod with the distance r .

As can be seen from diagram in Figure 28, the hardness of CVC NiTi rod is very constant in the direction of its radius. On the edge (0) of CVC NiTi rod the hardness is app. 550 HV and the hardness value is then slightly increasing and alternating to the middle of the rod ($D/2$), where the hardness value is app. 600 HV. It can be concluded that the difference in temperature during cooling between the edge and the middle of CVC NiTi rod does not affect the hardness significantly. As mentioned before, we used a smaller tip to measure hardness. This means that the differences in measured values of the hardness can be greater as the tip captures a smaller area.

Material with hardness 550–600 HV can be assumed to be very hard. Motemani et al. [89] measured the hardness of 50,7 NiTi to be over 500 HV when it was cooled rapidly with water, while the same material had hardness below 400 HV if it was cooled slowly in furnace. Also higher Ni content means higher hardness [90]. From this it can be concluded that over 550 HV

hardness of CVC NiTi rod is comprehensible due to its high Ni content (60 at. %) and fast water cooling during drawing.

4.3.2 Tensile Test

The picture of test specimens before and after the tensile test is seen in Figure 29. As mentioned before, CVC NiTi rod is very hard and as such very difficult to be processed. We had a lot of problems finding a contractor who had the appropriate tools for turning and grinding such hard materials. And even they had a lot of problems with the processing of the test specimens. After the machining of the CVC NiTi rod, the surfaces of the test specimens for the tensile test were still slightly rough, they did not have constant diameter along the entire length and there was practically no difference in diameter between the tearing part and the thread. So, it is not surprising that the fracture of test specimens occurred in the thread part where the test specimens are the weakest. Also the fracture was typically brittle (no neck has occurred).



Figure 29: A test specimen of CVC NiTi rod before and after the tensile test.

The tensile test diagram (Figure 30) shows a typical curve for brittle materials. Test 1 has a fracture tension, $\sigma_{T,u}$, of 388 MPa, a fracture strain, $\epsilon_{T,u}$, of 0.9 %, and an elastic modulus in tension, $E_{m,T}$, of 40 GPa, while test 2 has a fracture tension of 347 MPa, a fracture strain of 0.8 % and an elastic modulus in tension of 44 GPa. Both curves have a fairly linear shape up to the fracture. This means that the entire curves are located in an elastic region where the deformations are completely recoverable upon removal of the load. Such a diagram does not have a non-linear plastic region where deformations become permanent. If the material is sufficiently ductile, tensile stress can also greatly increase with high plastic deformation. CVC NiTi strand does not reach the plastic deformation and is thus unsuitable for strain hardening.

The obtained results correspond to the literature [85, 89, 90], where the authors determined that the brittleness of the as-cast NiTi alloy is mainly influenced by the high cooling rate of the alloy and its higher nickel content. If the as-cast NiTi alloy is furnace cooled or later hot worked, it also shows ductile properties.

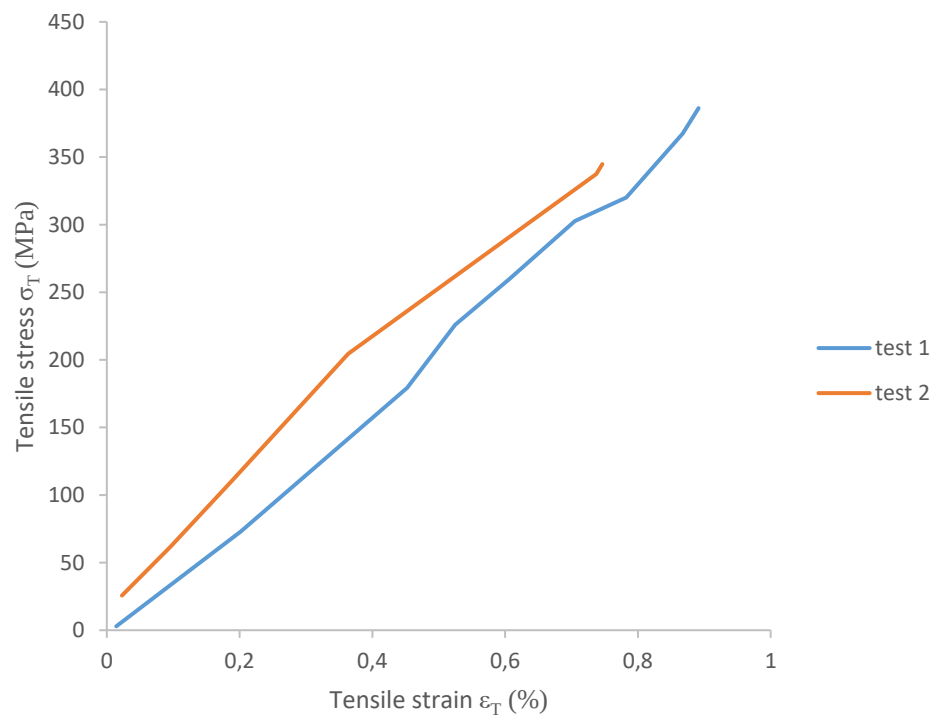


Figure 30: Stress-strain curve for tensile test of both test specimens of CVC NiTi rod.

4.3.3 Compressive Test

In contrast to the tensile test, where the specimen withstands tensile loads and is thus elongated, by the compressive test the specimen resists to compressive strength and is thus pushed together. Figure 31 shows the specimen before and after the compressive test. Before the test, we had a cylinder-shaped specimen that was crushed to a large number of small pieces after the achieved ultimate compressive strength.



Figure 31: A test specimen of CVC NiTi rod before and after compressive test.

The diagram in Figure 32 shows the curves of brittle material in the compressive test. Test 1 has the ultimate compressive strength, $\sigma_{C,u}$, of 2350 MPa, the ultimate compressive strain, $\varepsilon_{C,u}$, is 10.5%, the elastic modulus in compression, $E_{m,C}$ is 29 GPa, and test 2 has the ultimate compressive strength of 2380 MPa, the ultimate compressive strain of 11.5%, and elastic modulus in compression of 27 GPa. Both curves are very similar, and again they are located in the elastic area of the compressive test. Unlike the tensile test, this time there is a slight plastic plateau above 2000 MPa. The compressive test also shows that the CVC NiTi rod is brittle and is practically incapable of plastic deformations, and is therefore unsuitable for strain hardening.

The measured ultimate compressive strength is much higher than the fracture tension. This could be due to the fact that during the tensile test, the test specimen fractured in the thread and therefore the fracture tension should be much higher. On the other hand, there are some statements [90, 91] that the ultimate compressive strength is higher than the fracture tension in brittle materials, but it should be about the same order in metallic materials.

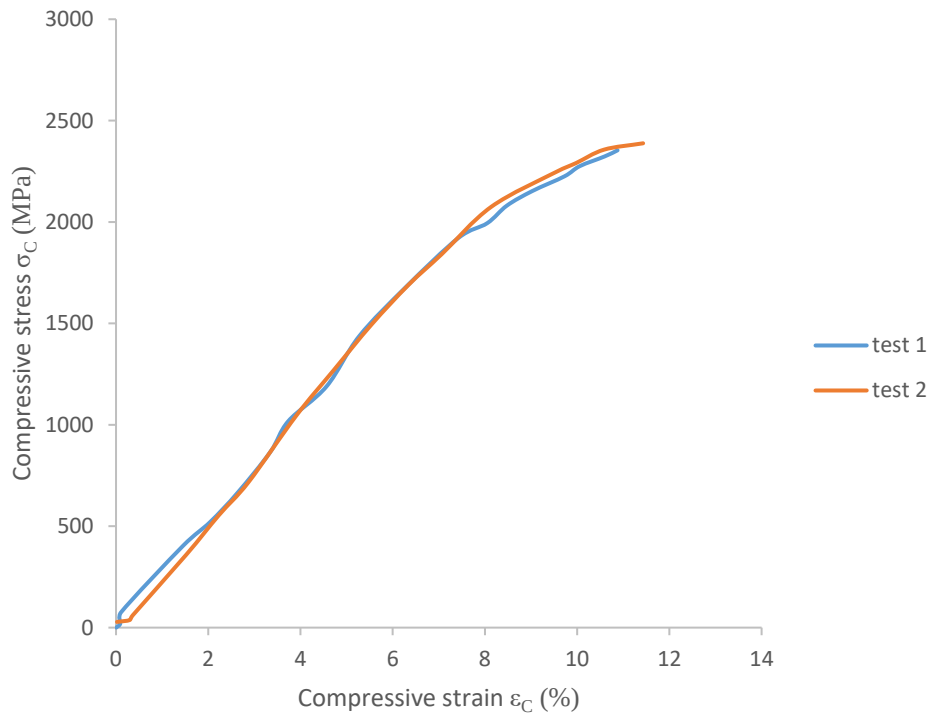


Figure 32: Stress-strain curve for compressive test of both test specimens of CVC NiTi rod.

4.3.4 4-point Bending Test

Figure 33 shows cylindrical test specimen with a diameter of 4 mm before and after the bending test. During a 4-point bending test, a brittle fracture occurred at about half the length of the test specimen.

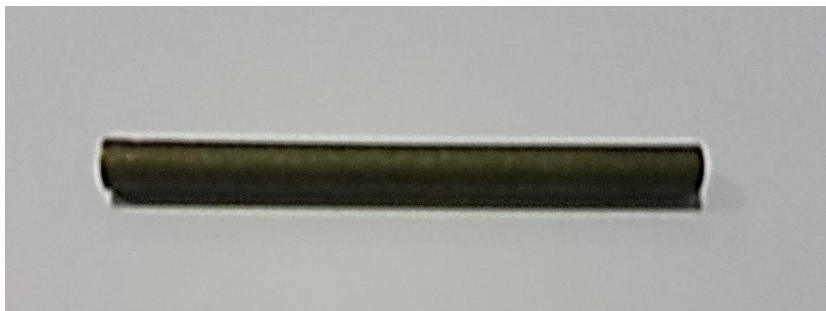




Figure 33: A test specimen of CVC NiTi rod before and after the 4-point bending test.

The 4-point bending diagram in Figure 34 shows predominantly linear curves. As expected, the curves are located in the elastic area. This time the fracture again occurs before the curves reach the area of plastic deformation. Test 1 has the ultimate flexure stress, $\sigma_{F,u}$, of 427 MPa, ultimate flexure strain, $\varepsilon_{F,u}$, of 0.5 % and elastic modulus in flexure, $E_{m,F}$, of 113 GPa. Test 2 has ultimate flexure stress of 610 MPa, ultimate flexure strain of 0.6 % and elastic modulus in flexure of 126 GPa. Test 3 has ultimate flexure stress of 520 MPa, ultimate flexure strain of 0.6 % and elastic modulus in flexure of 110 GPa.

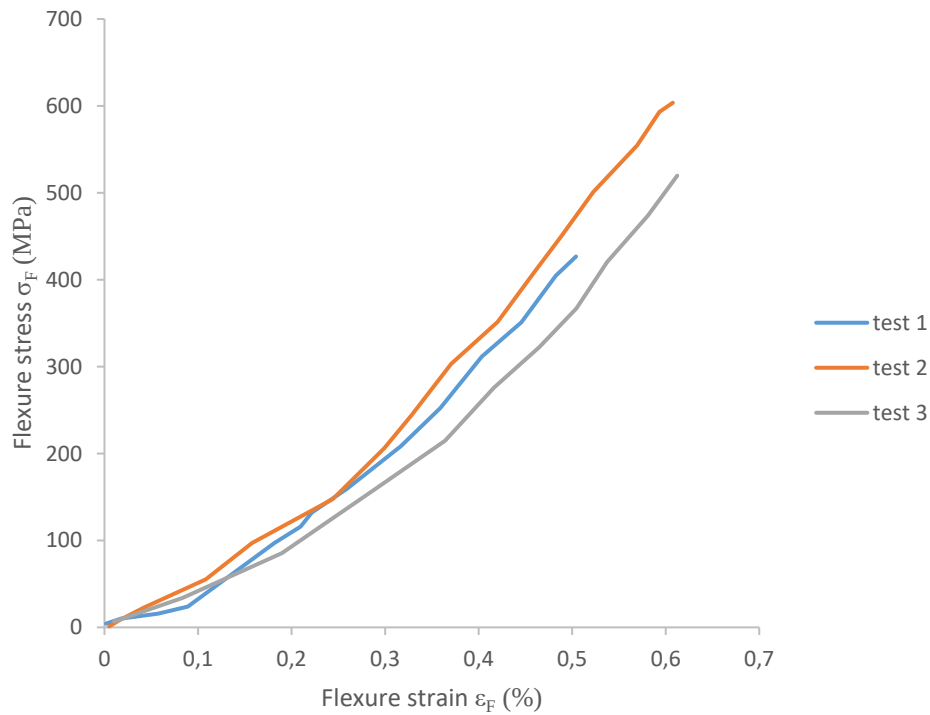


Figure 34: : Stress-strain curve for 4-point bending test of three test specimens of CVC NiTi rod.

4.4 ALD TiO₂ Thin Layer Deposition

Using the ALD method, we wanted to deposit a 50-nm-thick TiO₂ layer. After 1100 repeated cycles, the average thickness of the TiO₂ layer for CVC NiTi rod was 52.2 nm, and for the commercial NiTi was 51.7 nm (Figure 35).

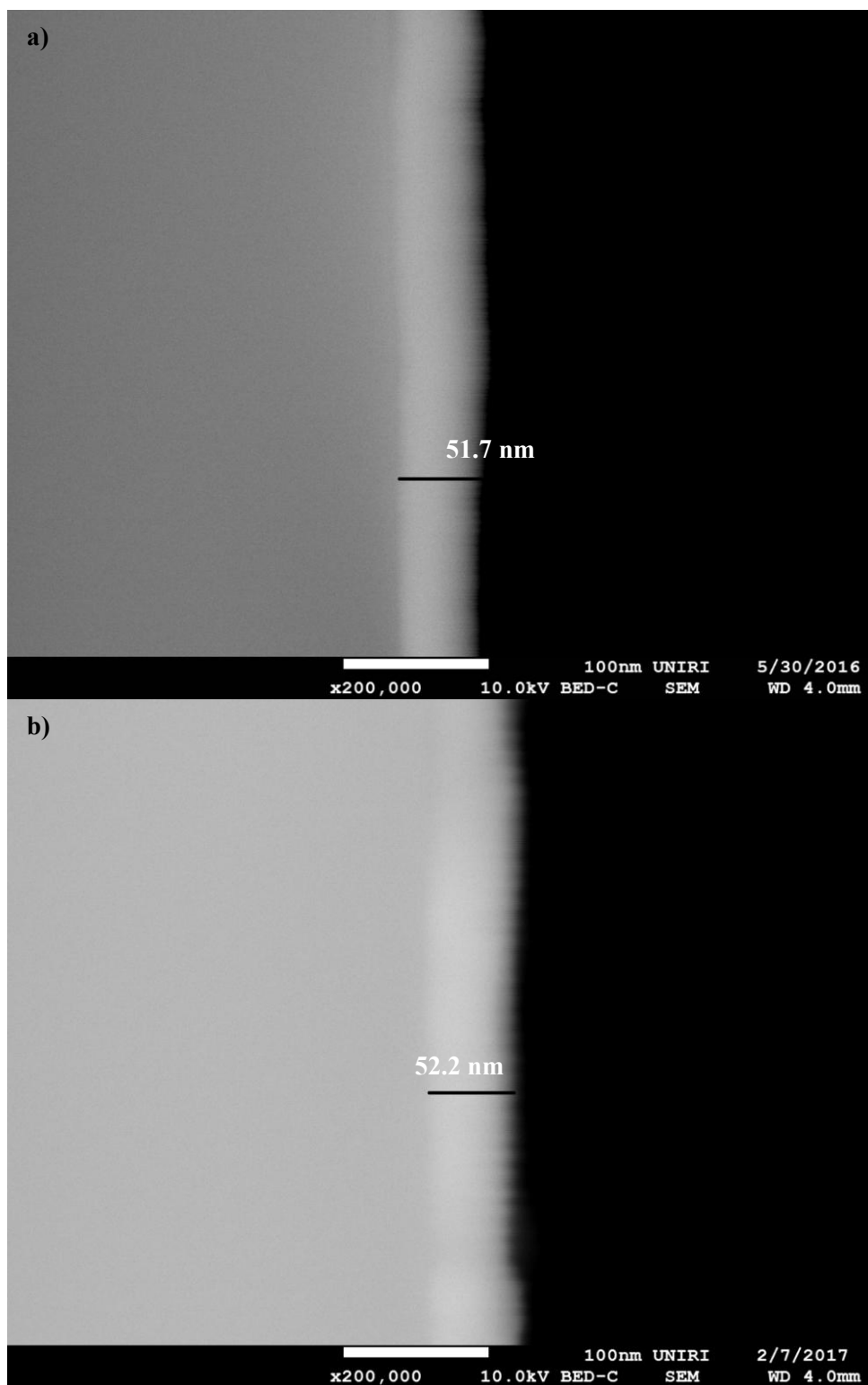


Figure 35: Secondary electron image at 200000 $\times$ magnification of cross-section of a) commercial NiTi and b) CVC NiTi rod to measure TiO₂ layer thickness.

As seen in Figure 36, the deposited TiO₂ layer is quite similar on both surfaces (CVC NiTi rod and commercial NiTi). The particles are quite different in size (from 50 nm to 1 μ m), while their shape is fairly tetrahedral with quite pointed edges, and the grain boundaries are clearly visible. Figure 37 shows a typical XPS analysis of TiO₂. Because the diagrams of TiO₂ deposited to the CVC NiTi rod and commercial NiTi are very similar, only 1 case is shown. The main peaks that

demonstrate the formation of TiO_2 on the surface of the sample are $\text{Ti}2p$ at binding energy of 469.2 eV and $\text{O}1s$ at binding energy of 530.7 eV. Because the ratio of intensities between 1Ti and 2O is about 1: 2, the deposited layer on the surface of the samples is actually TiO_2 [92, 93].

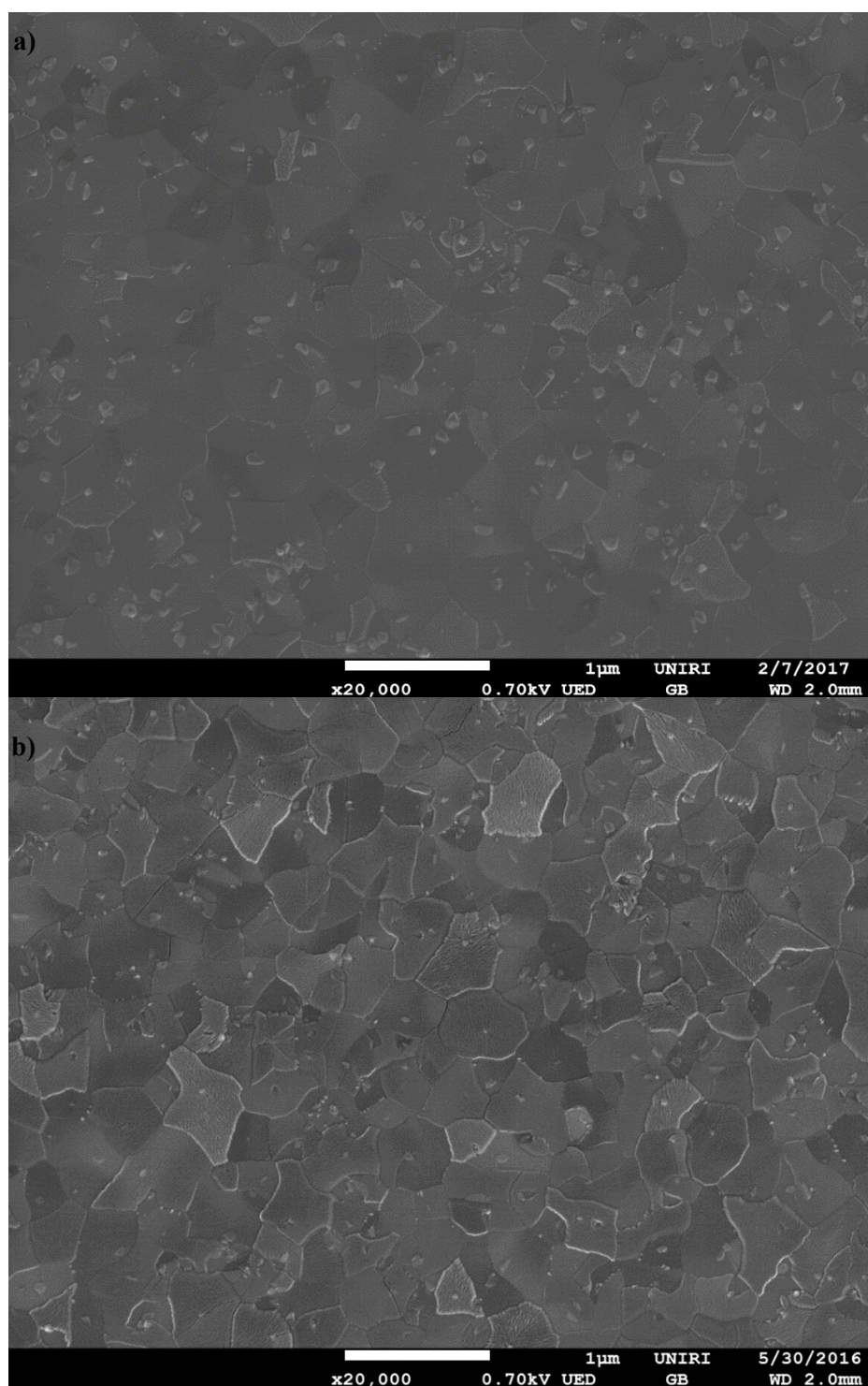


Figure 36: Secondary electron image at 20000 $\times$ magnification of TiO_2 layer on the surface of: a) CVC NiTi rod and b) commercial NiTi.

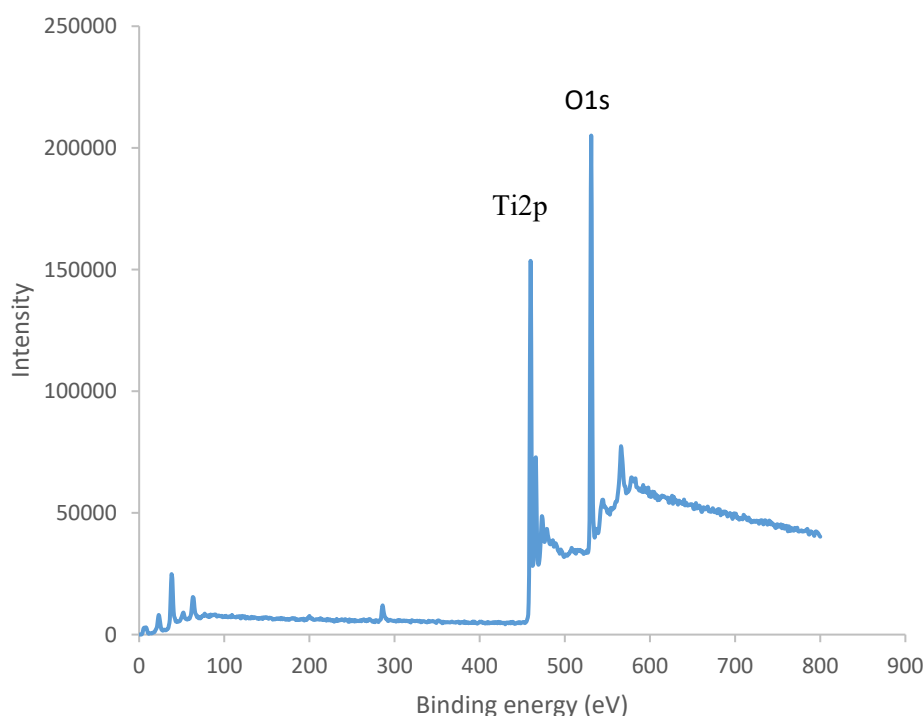


Figure 37: XPS spectra of TiO_2 .

4.5 Biocompatibility of CVC NiTi Rod

Biocompatibility is a very wide concept, but in its very essence it is the ability of a material not to cause any harm when it comes into contact with living tissue. The biocompatibility of biomaterials indicates their capability to induce cancer development (carcinogenicity), tissue or cell death (cytotoxicity), and protect against certain reactions (pyrogenicity and allergenicity), blood clotting (thrombogenicity), or genetic damage (mutagenicity) [94]. We have verified the cytocompatibility of the CVC NiTi rod. For this purpose, the samples were submersed in a HUVEC cells solution, where the HUVEC cells adhered to the samples surface. HUVEC cells are typical cells in blood vessels, especially veins.

Figure 38 shows the diagram of all the adhered HUVEC cells on the surface of: CVC NiTi rod, CVC NiTi rod covered with a 50-nm layer of TiO_2 , commercial NiTi and commercial NiTi coated with a 50-nm layer of TiO_2 . The number of adhered HUVEC cells on the surface of the CVC NiTi rod is $3124/\text{mm}^2$, on $\text{TiO}_2/\text{CVC NiTi}$ rod $4357/\text{mm}^2$, commercial NiTi $5524/\text{mm}^2$ and $\text{TiO}_2/\text{commercial NiTi}$ $5617/\text{mm}^2$. It can be seen that the number of HUVEC cells adhered to the surface of the commercial NiTi is higher than on the surface of the CVC NiTi rod. The influence of the 50-nm TiO_2 layer is more noticeable for the CVC NiTi rod as the number of adhered HUVEC cells is $1200/\text{mm}^2$ higher than if CVC NiTi rod does not have a TiO_2 layer. The difference is much smaller with commercial NiTi, where there are about 100 more adhered HUVEC cells $/\text{mm}^2$ if it is coated with a TiO_2 layer.

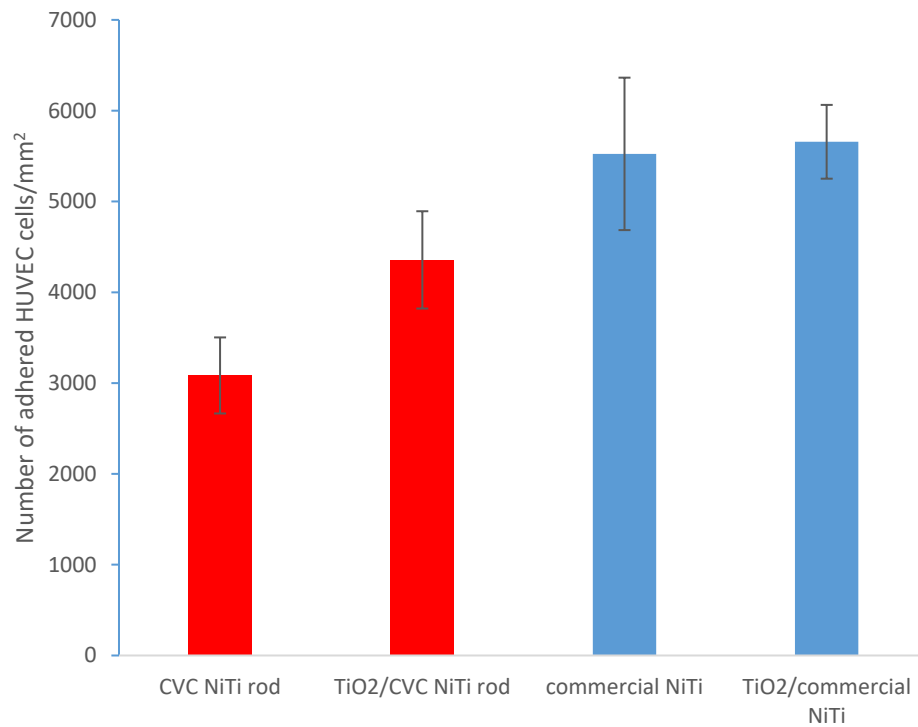


Figure 38: Number of adhered HUVEC cells on the surface of: CVC NiTi rod, TiO₂/CVC NiTi rod, commercial NiTi and TiO₂/commercial NiTi.

In Figure 39, the number of dead HUVEC cells is shown. The number of dead HUVEC cells on the surface of the CVC NiTi rod is 106 /mm², on the TiO₂/CVC NiTi rod it is 89 /mm², commercial NiTi it is 91 /mm² and TiO₂/commercial NiTi it is 66 /mm². The absolute number of dead HUVEC cells is the highest for CVC NiTi rod and the lowest for commercial NiTi covered with a TiO₂ layer. We can calculate the percentage of viable cells using:

$$\text{Viable HUVEC cells (\%)} = \left(1 - \frac{\text{Number of dead HUVEC cells}}{\text{Number of HUVEC cells}}\right) * 100 \quad (6).$$

In Table 3 are the results. It can be seen that the TiO₂/commercial NiTi has the highest percentage of viable cells (98,8), commercial NiTi 98,4 %, TiO₂/CVC NiTi rod 98,0 % and CVC NiTi rod with the lowest percentage of viable cells (96,6).

Table 3: Percentage of viable HUVEC cells on the surface of: CVC NiTi rod, TiO₂/CVC NiTi rod, commercial NiTi and TiO₂/commercial NiTi.

	Viable cells (%)
CVC NiTi rod	96.6
TiO ₂ /CVC NiTi rod	98.0
Commercial NiTi	98.4
TiO ₂ /commercial NiTi	98.8

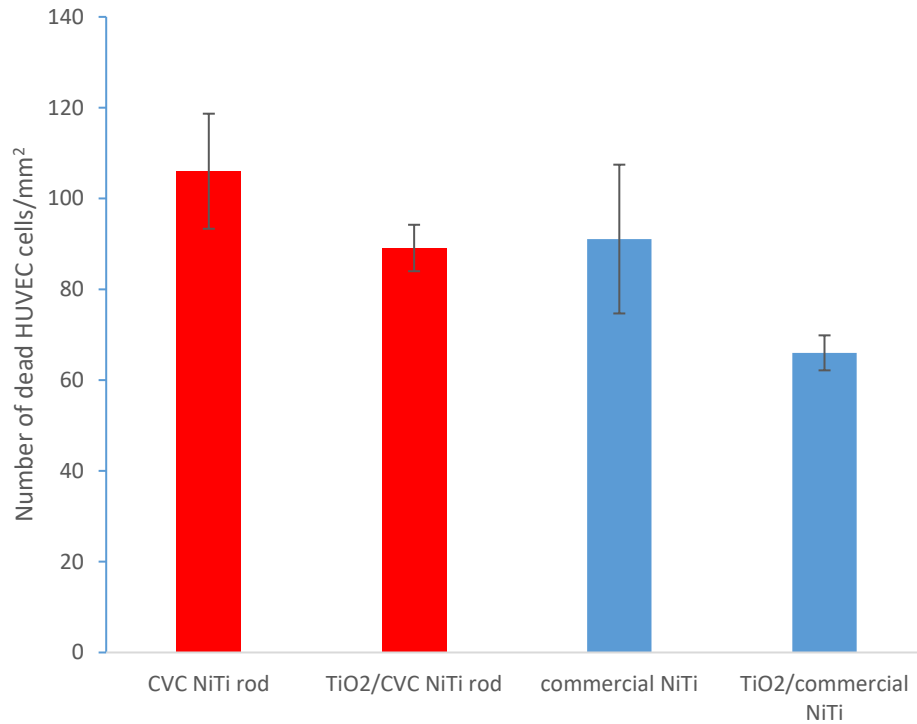


Figure 39: Number of dead HUVEC cells on the surface of: CVC NiTi rod, TiO₂/CVC NiTi rod, commercial NiTi and TiO₂/commercial NiTi.

Optical microscope images (Figure 40) of HUVEC cells on various substrates show that the cells are arranged individually on all substrates, and they are nowhere grouped together. On commercial NiTi, the cells are much more elongated, while on CVC NiTi rod they are much more scrunched together. In combination with Figure 41 showing a percentage of covered surface area with HUVEC cells, it can be seen that the most occupied area with HUVEC cells is on TiO₂/commercial NiTi (23,7 %), followed by commercial NiTi (23,1 %), TiO₂/CVC NiTi rod (20,1 %), and the least on the CVC NiTi rod (13,2 %).

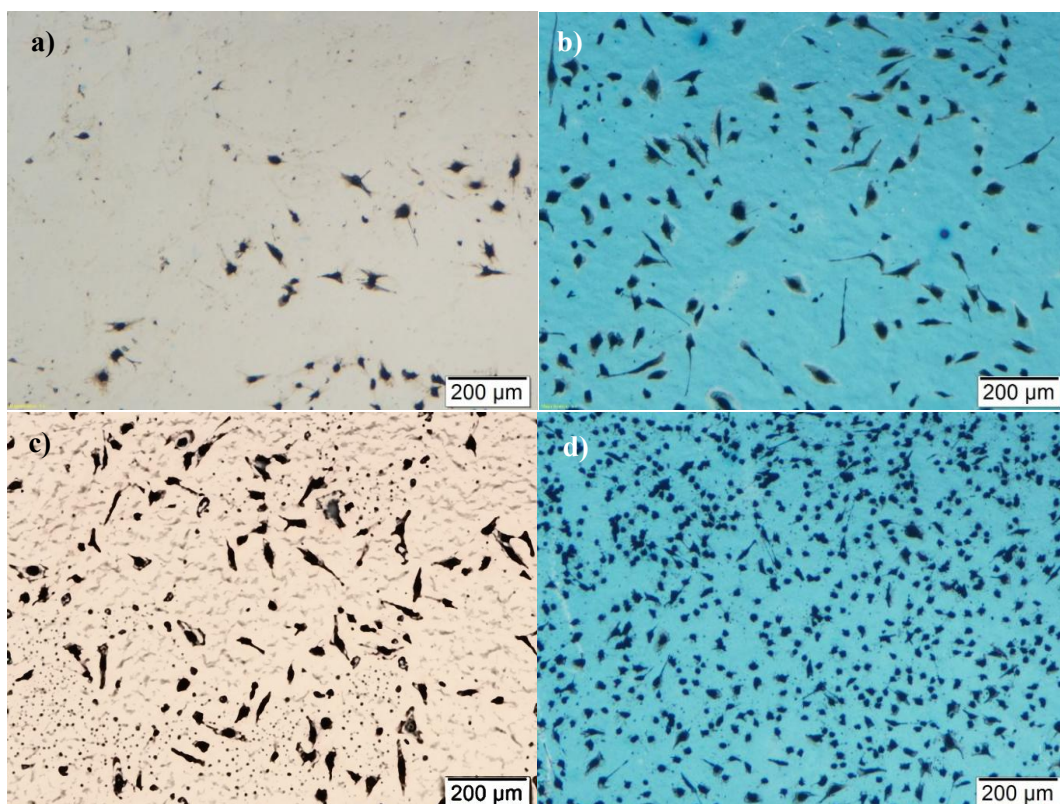


Figure 40: Optical microscope images of HUVEC cells on a) CVC NiTi rod, b) TiO_2 /CVC NiTi rod, c) com. NiTi and d) TiO_2 /com. NiTi.

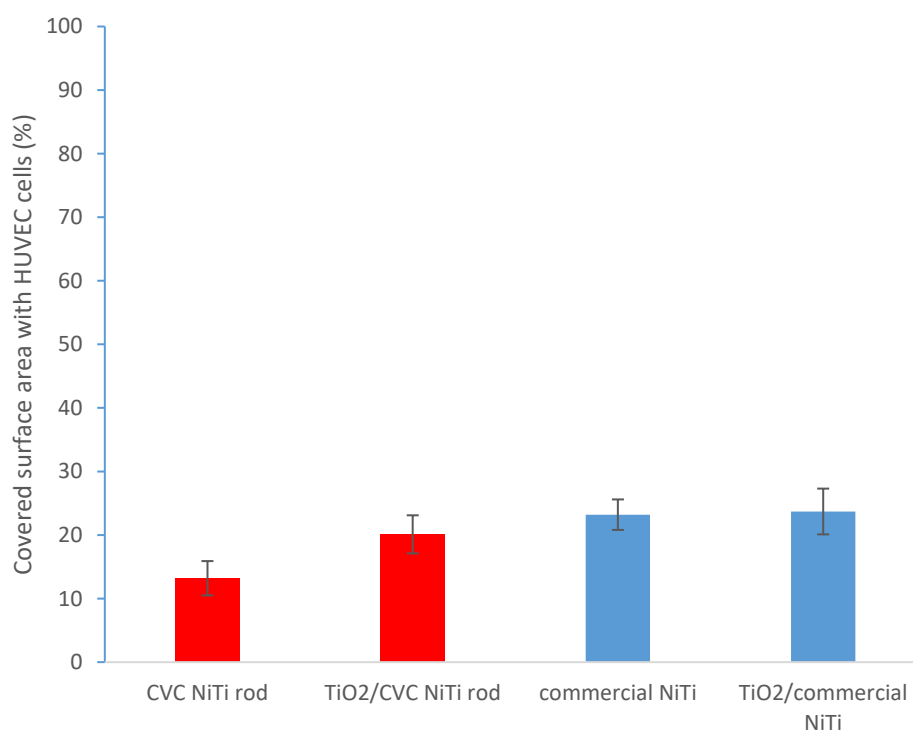


Figure 41: Covered surface area with HUVEC cells of: CVC NiTi rod, TiO_2 /CVC NiTi rod, commercial NiTi and TiO_2 /commercial NiTi.

Commercial NiTi coated with a 50-nm layer of TiO₂ is the most biocompatible. It has the most HUVEC cells adhered to its surface, the least dead HUVEC cells, the highest proportion of viable cells and the highest proportion of the surface area covered with HUVEC cells. Only slightly less biocompatible properties is shown by the commercial NiTi and CVC NiTi rod covered with a 50-nm TiO₂ layer. Far away from the other deviates CVC NiTi rod, which has practically 2 times less adhered HUVEC cells on its surface and also almost 2 times more dead HUVEC cells than the other samples. The literature review [95-99] explains that the growth of cells on the surface of nitinol is influenced by nickel and oxidation of the nitinol surface. The higher the concentration of nickel, the lower are biocompatible properties due to possibility of releasing of Ni ions that may cause toxic, allergic, and potentially carcinogenic effects [95], while biocompatibility can be improved with oxidation, as the TiO₂ layer is formed and thus the nickel is removed from the surface. Commercial NiTi (50Ni50Ti) has better biocompatibility due to the fact that it contains less nickel than the CVC NiTi rod (60Ni40Ti). On the other hand, a CVC NiTi rod coated with a TiO₂ layer on its surface has significantly improved biocompatibility. Another important factor is the oxidation of the nitinol surface. Free Gibbs energy of the TiO₂ formation is 4 times lower than for the formation of NiO, therefore TiO₂ is preferably formed on the surface of nitinol. But the thickness of TiO₂ layer cannot go into infinity. For thicknesses above 150 nm, the surface of nitinol is so depleted with titanium so that nickel begins to form aggregates. These growing aggregates create local tensions in the TiO₂ coating and results in the cracking of the TiO₂ coating and consequently the leakage of Ni occurs [44].

4.6 Corrosion Tests

4.6.1 Potentiodynamic Test

Figure 42 shows the potentiodynamic curves for different samples: CVC NiTi rod, commercial NiTi (com. NiTi), CVC NiTi rod with a 50-nm TiO₂ layer (TiO₂/CVC NiTi rod) and commercial NiTi with a 50-nm TiO₂ layer (TiO₂/com NiTi). All the measurements were carried out in Hank's solution at body temperature (37 °C). The electrochemical parameters of the potentiodynamic test are shown in Table 4. Corrosion potential and current, and breakdown potential and current values were obtained by graphic extrapolation. The corrosion potential is the highest for TiO₂/com. NiTi (-185.9 mV), which means that the passive layer on this sample is the most stable and resistant to external influences. This is followed by samples of TiO₂/CVC NiTi rod, CVC NiTi rod and com. NiTi. After the Tafel region, where the curve begins to rise steeply, a passive region begins that lasts to the breakdown potential. In the passive region a passive layer is formed on the samples. The wider the passive region, the more corrosion resistant the material is. The smallest passive range has a CVC NiTi rod (from -100 mV to 330 mV, which is 430 mV), followed by TiO₂/CVC NiTi rod (650 mV), com. NiTi (730 mV) and TiO₂/com. NiTi. The lowest breakdown potential has CVC NiTi rod (329.2 mV), followed by com. NiTi (633.8 mV) and TiO₂/CVC NiTi rod (642.5 mV), while TiO₂/com. NiTi does not reach the breakdown potential in the measurement range. As already the name suggests, this passive layer breaks down at this potential, which enables the formation of pits on the surface. This is also accompanied by a rapid increase in anode current due to the passivity breakdown [100]. The corrosion rate is thus the smallest for TiO₂/com. NiTi, far away, but very close together are the TiO₂/CVC NiTi rod and com. NiTi, while CVC NiTi rod shows the highest corrosion rate, or the lowest corrosion resistance by potentiodynamic test.

Table 4: Electrochemical parameters determined from the potentiodynamic curves.

	E_{corr} (mV)	I_{corr} (μA)	E_{bd} (mV)	I_{bd} (μA)	Corrosion rate (mmpy)
CVC NiTi rod	-334.1	0.4423	329.2	6.77	$4.201 \cdot 10^{-3}$
com. NiTi	-299.9	0.298	633.8	6.148	$2.628 \cdot 10^{-3}$
TiO ₂ /CVC NiTi rod	-234.6	0.335	642.5	6.234	$3.113 \cdot 10^{-3}$
TiO ₂ /com. NiTi	-185.9	0.163	/	/	$1.114 \cdot 10^{-4}$

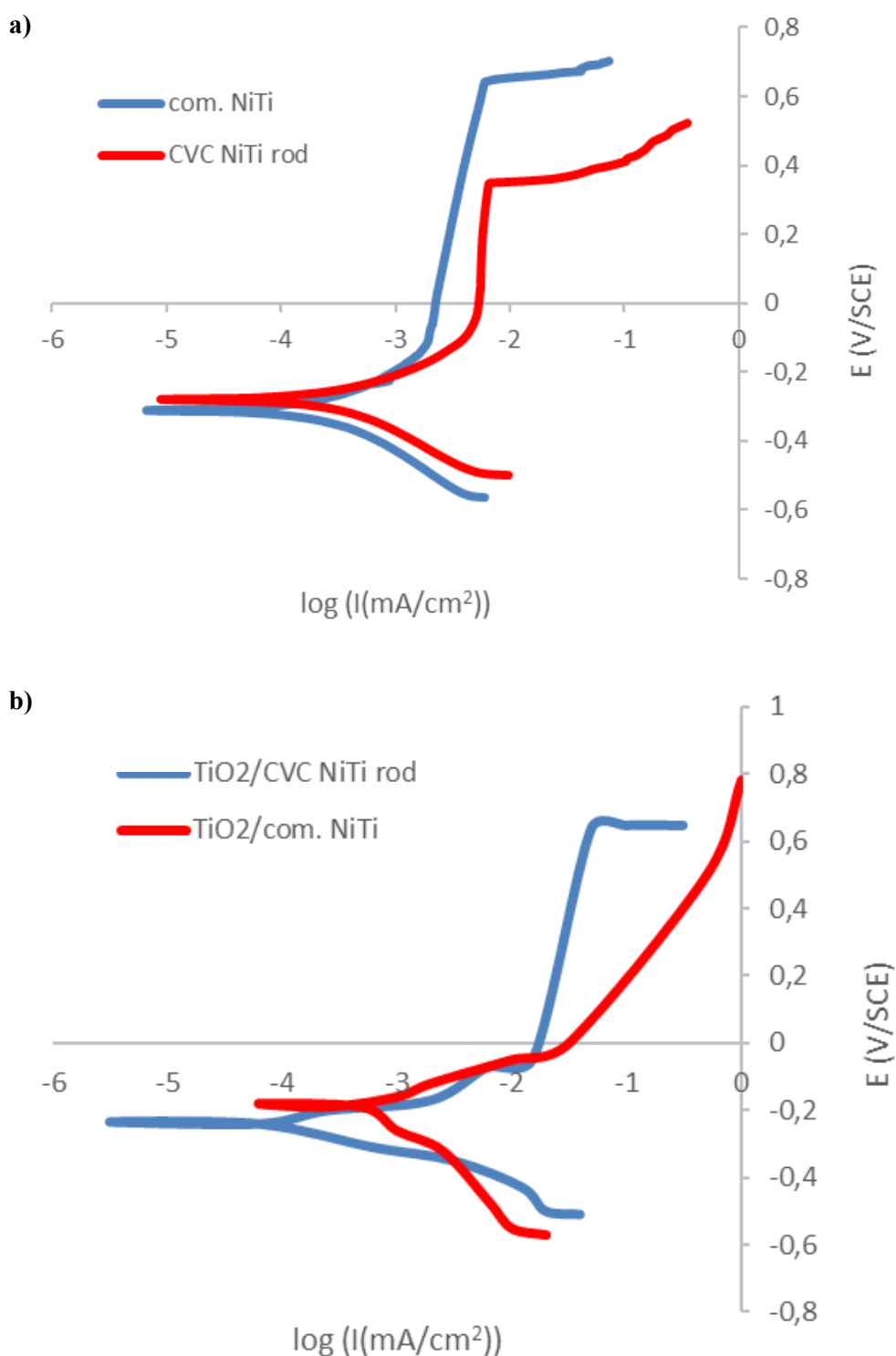


Figure 42: Potentiodynamic curves for: a) CVC NiTi rod and com. NiTi and b) TiO₂/CVC NiTi rod and TiO₂/com. NiTi.

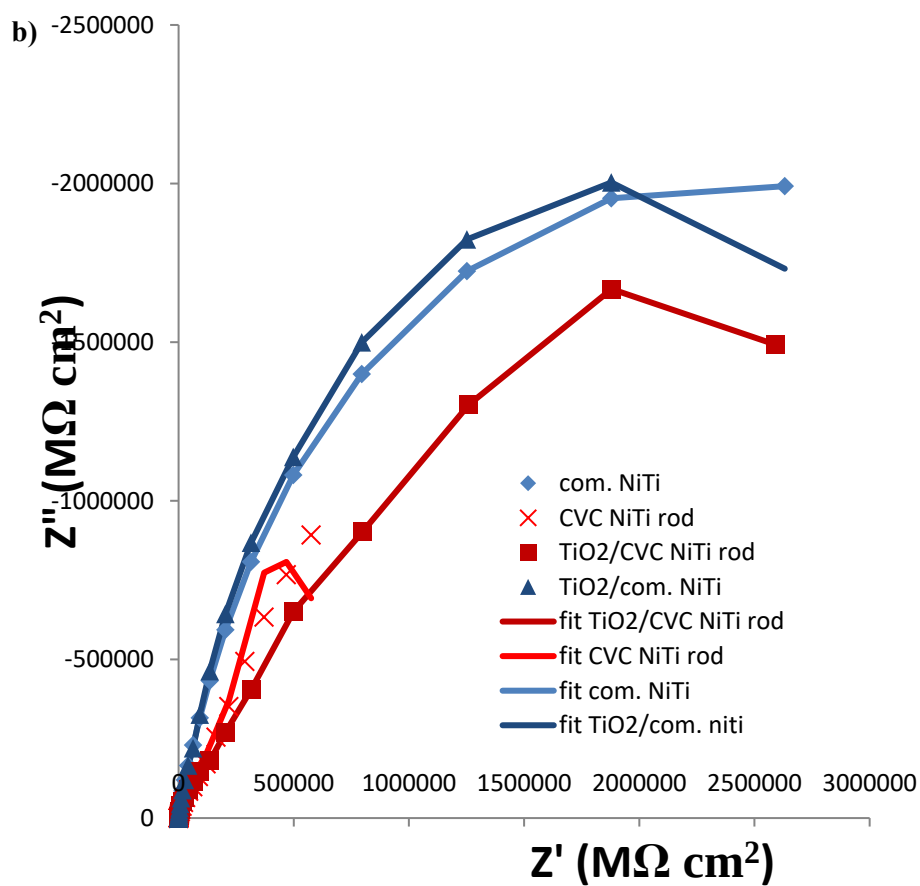
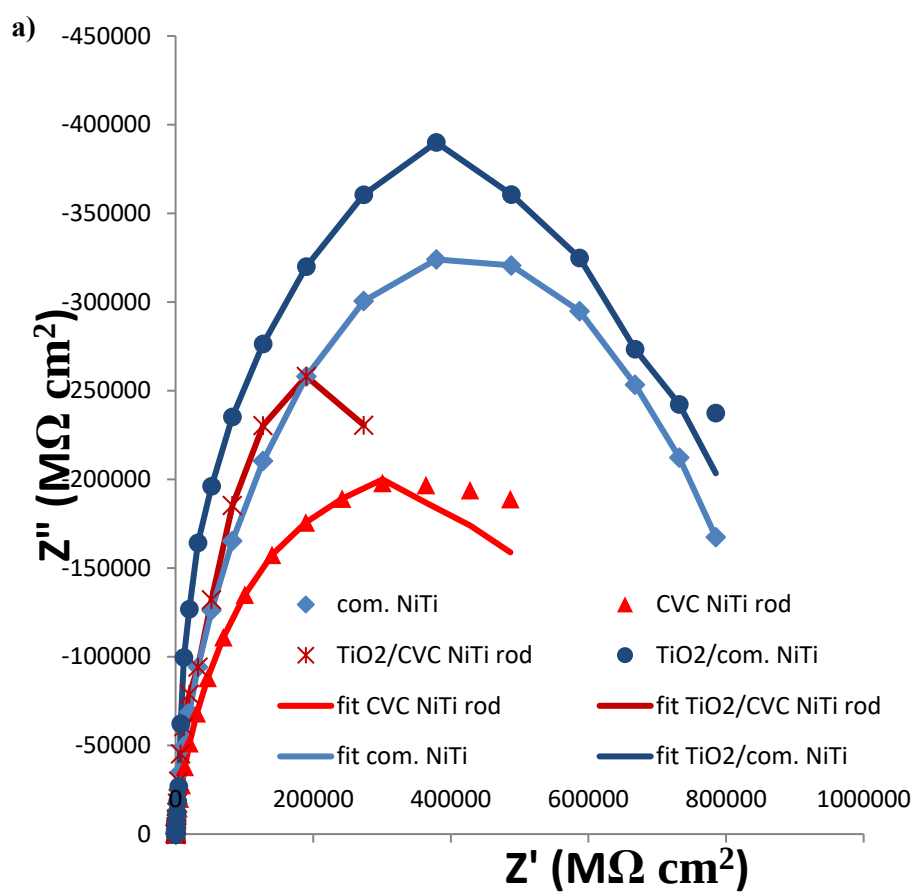
4.6.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit potential conditions in a simulated physiological fluid for 8 days. Figure 43 shows the Nyquist impedance diagrams for the CVC NiTi rod, commercial NiTi and also for both with a deposited 50-nm TiO₂ layer at different times of immersion. The system response, shown through the

Nyquist plots, shows a typical depressed semicircle shape, and the response is increasing with the immersion time for all samples.

The analysed data for Nyquist plots predicted the equivalent circuits shown in Figure 44. For inhomogeneous layers, similar equivalent circuit was applied by Izquierdo J. et al. [101] and Figueira N. et al. [102]. R_1 represents the resistance through the porous external oxide layer, while R_2 represents the resistance through the inner compact oxide layer. R_s is the resistance of the solution, while CPE_1 and CPE_2 are constant phase elements corresponding to R_1 and R_2 . The use of a constant phase element (CPE) was required to consent the non-ideal capacitive response observed as a depressed semicircle in the corresponding Nyquist diagrams. The CPE originates from the surface roughness and inhomogeneities present in the titanium oxide layers at the microscopic level [101]. The equivalent circuit in Figure 44a has only a resistance through the oxide layer and was used only for the samples of CVC NiTi rod and commercial NiTi in the first 48 h of immersion. After this exposure time, the equivalent circuit in Figure 44b was applied, and this equivalent circuit was also valid for all the immersion times for TiO_2 /CVC NiTi rod and TiO_2 /commercial NiTi. The difference can be explained by not having an oxide layer at the beginning on the surface of CVC NiTi rod and the commercial NiTi. Therefore, for the first 48 h of immersion, the resulting layer is still very thin and compact, which can be represented by only 1 resistor. After this time, the oxide layer becomes thicker and inhomogeneous, so another resistance is added, which represents the resistance through the porous oxide layer. On the surface the TiO_2 /CVC NiTi rod and the TiO_2 /commercial NiTi samples, a 50-nm TiO_2 layer was deposited previously with ALD, so an equivalent circuit with two resistances was used from the beginning of the immersion.

Table 5 shows the resistance values of the porous layer (R_1) and the oxide layer (R_2) for all the samples. The CVC NiTi rod and the commercial NiTi have for the first 48 hours of immersion only a resistance through the oxide layer as a consequence of the thin and compact layer. After this time a resistance through the porous layer is also considered. TiO_2 /CVC NiTi rod and TiO_2 /commercial NiTi have the resistances through both layers all the time of immersion, since the TiO_2 layer was previously deposited to the surface of the samples. The resistance R_1 is considerably lower for all the samples, which is not surprising, since the solution will penetrate through the porous layer much more easily than through the compact layer. While the resistance through the oxide layer is increasing over the immersion time for all the samples, since the layer is getting thicker, the resistance through the porous layer is quite constant.



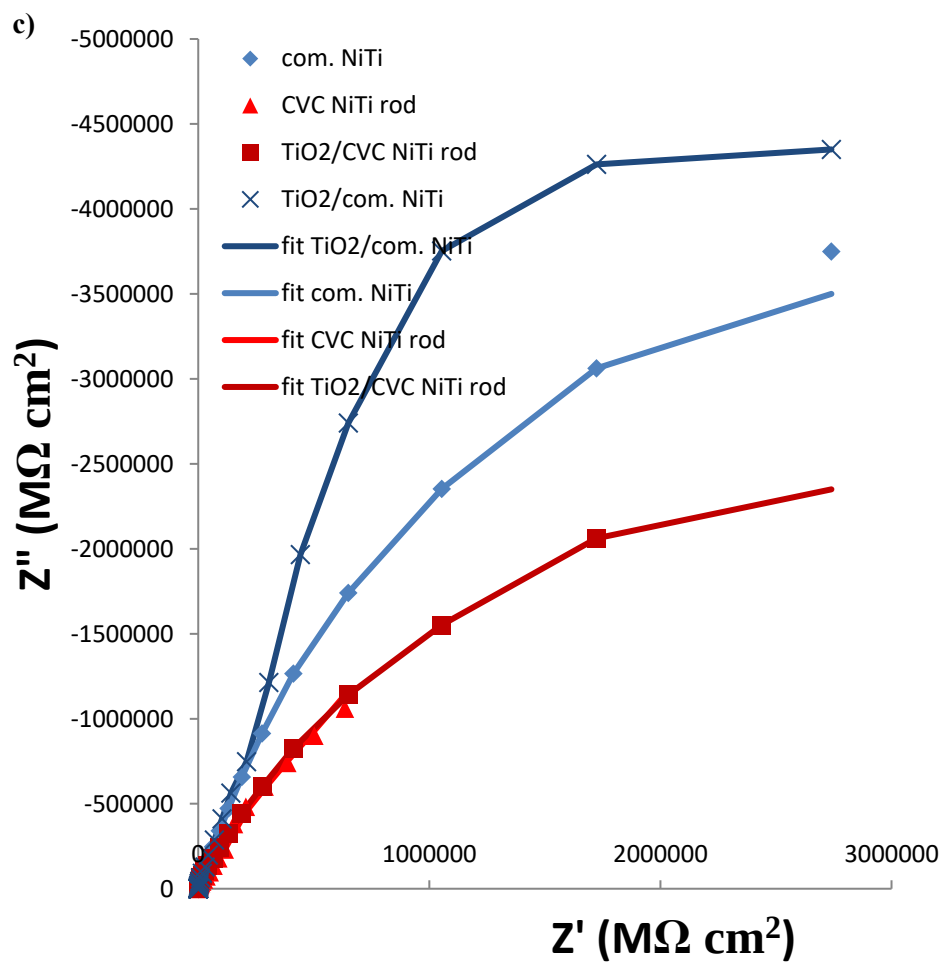
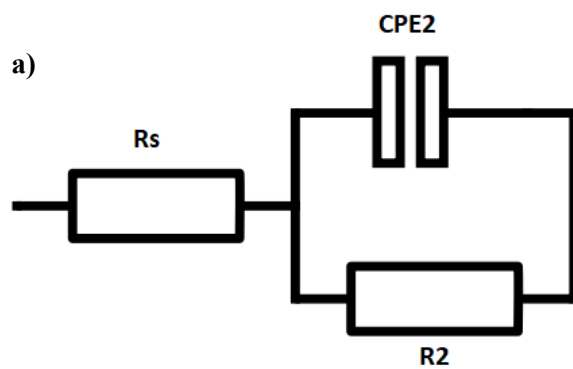


Figure 43: Nyquist diagrams for the CVC NiTi rod, commercial NiTi, TiO₂/CVC NiTi rod and TiO₂/commercial NiTi after a) 12 h, b) 96 h, and c) 168 h of immersion.



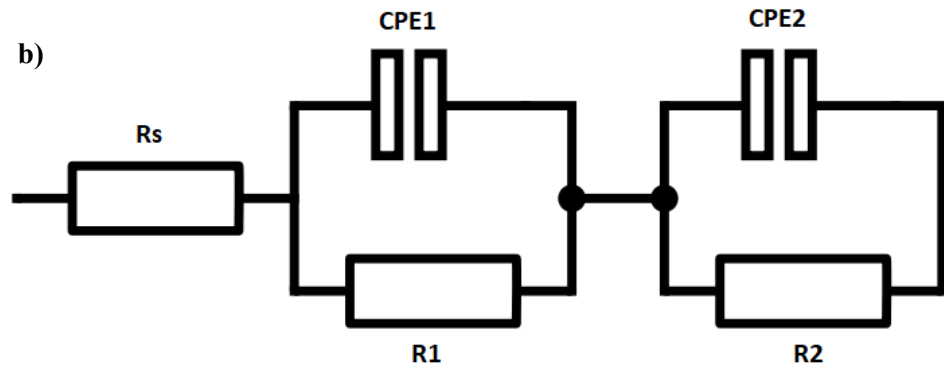


Figure 44: Equivalent circuits for the interpretation of the measured impedance spectra with: a) one resistance and b) two resistances.

Table 5: Porous corrosion resistance R_1 and oxide corrosion resistance R_2 of different samples at certain time of immersion.

t (h)	$R_{1com} * 10^5$ (Ω)	$R_{2com} * 10^5$ (Ω)	$R_{1CVC} * 10^5$ (Ω)	$R_{2CVC} * 10^5$ (Ω)	$R_{1TiO_2/CVC} * 10^5$ (Ω)	$R_{2TiO_2/CVC} * 10^5$ (Ω)	$R_{1TiO_2/com} * 10^5$ (Ω)	$R_{2TiO_2/com} * 10^5$ (Ω)
1	0.00	3.74	0.00	2.08	0.24	2.22	0.82	4.00
6	0.00	6.86	0.00	2.30	0.42	3.29	0.94	8.20
12	0.00	6.49	0.00	2.61	0.79	3.85	1.16	10.20
24	0.00	7.41	0.00	2.71	1.36	4.41	1.34	18.01
48	0.00	10.94	0.00	2.55	2.44	7.58	1.45	25.00
72	4.32	19.65	0.33	7.80	2.59	13.80	1.37	33.81
96	6.92	40.35	0.28	18.00	2.48	22.51	1.56	52.51
120	7.46	56.88	0.34	24.08	2.66	33.00	1.35	68.50
144	8.32	70.29	0.33	28.06	2.68	44.72	1.34	89.00
168	9.01	89.47	0.35	30.25	2.69	56.51	1.26	101.04
192	10.28	81.47	0.31	29.62	2.29	60.31	1.46	113.56

Figure 44 represents the polarization or the total corrosion resistance R_p as a function of time. R_p can be calculated according to equation:

$$R_p = R_1 + R_2 \quad (7)$$

The diagram of total corrosion resistance (Figure 45) clearly shows that the corrosion resistance increases with time for all 4 samples. This is a consequence of the formation of a protective oxide layer. It is also noticeable that in the case when the TiO_2 layer is deposited on the sample, the corrosion resistance is increasing in the initial time, while in the case of the CVC NiTi rod and commercial NiTi in the initial 48 hours there is no significant change in resistance as a consequence of the thin oxide layer. The highest corrosion resistance is for the TiO_2 /commercial NiTi, followed by the commercial NiTi and the TiO_2 /CVC NiTi rod, and the poorest corrosion resistance is for the CVC NiTi rod. The cause of the poorer corrosion properties of the CVC NiTi rod is inhomogeneity and a higher nickel content than in the commercial NiTi.

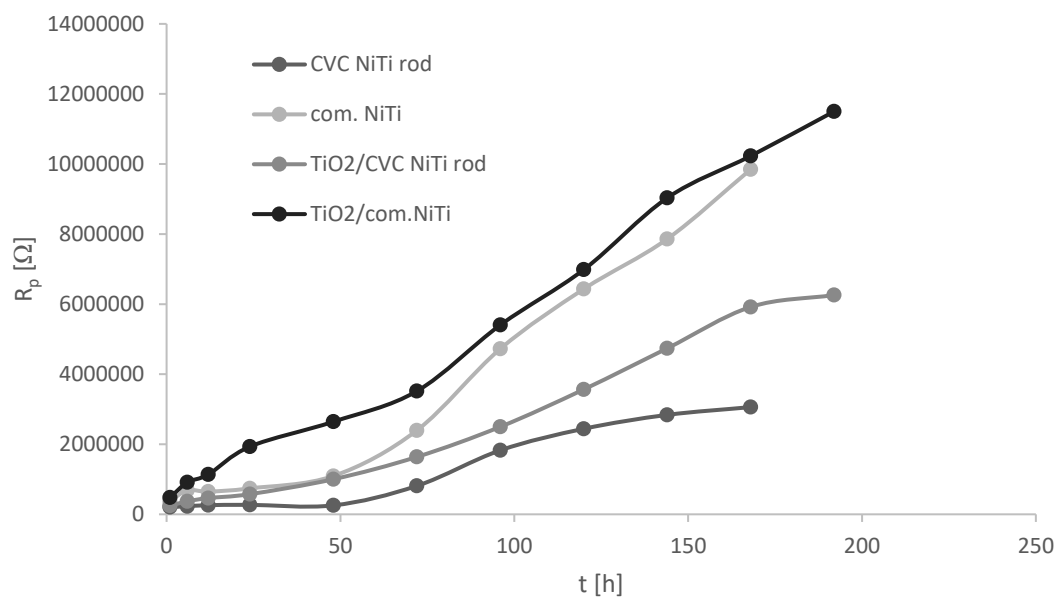


Figure 45: Total corrosion resistance vs time for different samples.

Chapter 5

Conclusions

5.1 Summary

In this doctoral work, the possibility of producing a NiTi alloy in the shape of rod, with the smallest diameter and a chemical composition of 50 at.% Ni and 50 at.%, using Vacuum Induction Melting and Continuous Vertical Casting was investigated. With the experiments we confirmed that it is possible to produce a NiTi rod with a diameter of 11.5 mm. The conclusions are as follows:

- the melting process of the NiTi rod can be carried out in the induction melting system using a clay graphite crucible, with the correct Ni and Ti storing, at a vacuum of at least 10^{-2} mbar, at $T = 1380^{\circ}\text{C}$ and with the appropriate temperature heating regime.
- The CVC casting of the NiTi rod is possible using the ZrO_2 nozzle, copper mould, clay graphite crucible, 1450°C melting temperature, 8 mm step, 0,5 s waiting time and 26 l/min mould cooling.
- The chemical composition of the CVC NiTi rod slightly deviates from the required 50:50 due to the non-optimal melting process and the measurement error of the chemical analyses. In the optimal casting, the achieved chemical composition of the CVC rod was: 52 at.% Ni, 48 at.% Ti.
- The microstructure of the as-cast NiTi rod is dendritic, with clearly visible grain boundaries. The primary phase is NiTi, while the binary lamellar eutectic consists of the NiTi eut + Ni_3Ti phase. EBSD analysis confirmed the chemical composition of the primary phase 50 at.% Ni and 50 at.% Ti and the chemical composition of the binary eutectic NiTi eut. (50/50) and Ni_3Ti .
- In some areas in the microstructure of CVC NiTi rod it contains individual inclusions of TiC as a result of the reaction between the titanium and the carbon from the clay graphite crucible during the melting process.
- Comparison of the microstructure of the CVT NiTi rod with a commercial Nitinol sheet shows that the commercial Nitinol has a typical microstructure resulting from the forming and is not comparable to the "as-cast" microstructure of NiTi rod.
- The hardness measurement of the as-cast CVC NiTi rod has revealed that it is very hard (> 550 HV), which is influenced by high cooling rates during CVC process and higher nickel content.
- The results of the tensile, compressive and bending tests in the form of diagrams evidently showed that the CVC NiTi rod breaks before it passes from the elastic to the plastic region. The CVC NiTi rod is therefore brittle material and cannot be strain hardened.

In the second part of the doctoral work, the possibility of using CVC NiTi rod for dental purposes was investigated. The results are as follows:

- Atomic Layer Deposition may serve as a method for improving surface properties in the cases where the material is intended to be used for biomedical purposes. With a 50-nm TiO_2 layer deposition on the selected samples surface of the CVC NiTi rod and the commercial NiTi some of the properties have improved significantly:
- The biocompatibility test with HUVEC cells showed that the most biocompatible is the commercial NiTi with a 50-nm TiO_2 layer because it has the most HUVEC cells adhered to its surface, the least dead HUVEC cells, the highest proportion of viable cells and the highest proportion of the surface area covered with HUVEC cells. Only slightly less biocompatible properties are exhibited by the commercial NiTi and CVC NiTi rod covered with a 50-nm TiO_2 layer. The least biocompatible rod is the CVC NiTi.
- Similarly, the best corrosion properties are seen for the commercial NiTi with a 50-nm TiO_2 layer, followed by relatively comparable properties of the commercial NiTi and the CVC NiTi rod covered with a 50-nm TiO_2 layer, and the least corrosion resistant is the CVC NiTi rod.
- The CVC NiTi rod contains more nickel than the commercial NiTi. Therefore, its corrosion and biocompatible properties are poorer than that of the commercial NiTi. If we could cast a CVC

NiTi rod with the desired chemical composition (50Ni50Ti), we would expect similar biocompatible and corrosion properties to the commercial NiTi

- A 50-nm layer of TiO_2 improves the corrosion and biocompatible properties of the CVC NiTi rod and the commercial NiTi. A significantly larger effect is observed for the CVT NiTi rod.

5.2 Future Work

- To produce a NiTi rod with a chemical composition close to 50Ni50Ti using Vacuum Induction Melting and Continuous Vertical Casting.

- Finding the optimal melting parameters (the right frequency of the induction for optimal mixing of the melt, melting temperature, etc.), vacuum conditions (high enough vacuum to avoid the oxidation of titanium, the right protective gas) and drawing parameters (to find the right time of the sequence for draw and pause).

- Replacing some used materials with less reactive ones (instead of an Fe starter bar, a Ti starter bar will be used, different nozzle material).

- Practically examine the influence of the solidification rate (or flow and temperature of the cooling water) on the microstructure and the mechanical properties of the rod. For this purpose, new cooling system will be used.

- Finding the minimum possible diameter of the rod, which could still be drawn.

5.3 Contribution to Science

Nitinol is difficult to cast due to titanium's high reactivity and viscosity, and good mechanical properties of the alloy, which complicates the option of further operations with the alloy. Today, nitinol is produced by melting nickel and titanium into the furnace, and then the hot casting is poured into a mould where it solidifies. After that nitinol is sent for further transformations. But we succeeded to produce nitinol by continuous casting. This means that we were melting nickel and titanium in the same furnace, from which directly, by using a drawing mechanism, a NiTi rod with diameter of 11 mm was pulled out. With this we saved on energy, costs and, especially, time. We also found that with the deposition of a titanium oxide layer, biocompatibility and the corrosion properties of NiTi rod are significantly improved; therefore, the use of titanium oxide as a protection is suitable for biomaterials. For the continuous vertical casting process of nitinol, we lodged a patent application.

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Publications Related to the Thesis

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- Stambolić A, Anžel I, Lojen G, Kocijan A, Jenko M, Rudolf R. Continuous Vertical Casting of a NiTi Alloy. *Materiali in tehnologije*. 2016;**50(6)**:981-988. doi: 10.17222/mit.2016.111.
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