

FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
TÜRKİYE



**STUDYING THE EFFECT OF TiO₂ COATING AND IMPROVING
BIOCOMPATIBILITY OF NiTiSn BIOMEDICAL SHAPE
MEMORY ALLOYS**

Ibrahim Nazem QADER

Doctoral Thesis

DEPARTMENT OF PHYSICS

Division of Solid State Physics

MAY 2021

FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
T Ü R K İ Y E

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Title:	Studying the Effect of TiO ₂ Coating and Improving Biocompatibility of NiTiSn Biomedical Shape Memory Alloys
Author:	Ibrahim Nazem QADER
Submission Date:	19 April 2021
Defense Date:	17 May 2021

THESIS APPROVAL

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I hereby declare that I wrote this Doctoral Thesis titled “Studying the Effect of TiO₂ Coating and Improving Biocompatibility of NiTiSn Biomedical Shape Memory Alloys” in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Firat University. I also declare that all information in it is correct, that I acted according to scientific ethics in producing and presenting the findings, cited all the references I used, express all institutions or organizations or persons who supported the thesis financially. I have never used the data and information I provide here in order to get a degree in any way.

17 May 2021

Ibrahim Nazem QADER



PREFACE

The investigation about shape memory behavior and biocompatibility of NiTi-based alloys is an important subject of study. Although they are used in many applications, there are still limitations that open gates for researchers.

All gratitude and blessings to Allah for the successful accomplishment of this study. I am grateful to Allah for all chances, difficulties, and energy that have been bestowed upon me in order to complete the thesis. During this process, I learned a great deal, not only academically but also personally.

I am very grateful to my supervisor, *Prof. Dr. Mediha KÖK*, for opening up so many ways of research on smart material and especially shape memory alloys. She also taught me ways to think and work as a group. I learned from her the meaning of patience and encouragement and how to behave with students properly. I hope in the future; I can do the same. “teşekkürler hocam”. Additionally, I would like to thanks my co-supervisor *Prof. Dr. Zehra Deniz ÇIRAK* for countless help.

Thanks to my parents for always paving the way for progress and for being the strength of my heart. Also, thanks to my brothers and sisters that are happy with my success. Besides, my lovely wife, *Kwestan Hussein AHMED*, and my sons, *Yousif, Dana*, and *Zana*, tolerated me and supported me for a long time.

Last but not least, I know that in these few lines I cannot name all the loved ones who are my colleagues, but with a few sentences, I try to point to a handful of goodies. My endless thanks to *Assoc. Prof. Dr. Fethi DAĞDELEN* behaves like a friend and I am proud to have learned so many valuable things from him. Also, thanks to all of my colleagues and classmates, including *Dr. Mustafa Ersin Pekdemir*, *Dr. Ercan ERCAN*, *Mrs. Ecem ONER*, *Mrs. Esra BALCI*, *Mr. Muhammed Sait KANCA*, *Mr. Safar Saeed MOHAMMED*, *Mrs. Meltem COŞKUN*, and *Mr. Shakhawan Salih ABDULLAH*.

This thesis was supported by project number **FF.20.06** by Firat University Scientific Research Projects Coordination Unit (FÜBAP).

Ibrahim Nazem QADER
ELAZIG, 2021

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ABSTRACT

Studying the Effect of TiO₂ Coating and Improving Biocompatibility of NiTiSn Biomedical Shape Memory Alloys

Ibrahim Nazem QADER

Doctoral Thesis

FIRAT UNIVERSITY
Graduate School of Natural and Applied Sciences
Department of Physics

May 2021, Page: xiv + 104

NiTiSn shape memory alloys have versatile applications based on their alloying element, composition, production technique, and other treating procedures. This study consists of two parts, in the first part Ni_{50-x}Ti₅₀Sn_x SMAs, and in the second part a wire formed Ni₄₇Ti₅₀Sn₃ alloy was investigated. Many different measurements were performed for the alloys, including differential scanning calorimetry, Vickers microhardness, XRD, SEM, and EDX. Also, The change in the microhardness and crystallite size of the alloys were in harmony. The martensite peaks and austenite troughs were moved to the lower temperature by increasing the number of cycling processes, additionally, the shifting rate was amplified by substituting more Ni with Sn element in the alloy.

In the second part, the impact of TiO₂ coating and some other biocompatible improvements in the NiTiSn wire-shaped SMAs was investigated. The as-cast and oxidized NiTiSn-wire SMAs were examined for their oxidation behavior, phase transformation, crystal structure, microstructure, and corrosivity. Besides, the in-vitro study for the as-cast and oxidized wire was carried out in simulated body fluid and physiological solution at body temperature. The corrosion rate of the as-cast SMA was 481 and 786 $\mu\text{m}/\text{year}$ in simulated body fluid and physiological serum, respectively, which is less than the value reported for an equiatomic NiTi SMAs. Consequently, It can be stated that NiTiSn-wire is highly biocompatible and may be used for various purposes such as implantation in the human body.

Keywords: Low-Temperature Shape Memory Alloy, NiTiSn; TiO₂, Phase transformation, Coating, Biocompatibility, Corrosivity

ÖZET

TiO₂ Kaplamanın Etkisinin İncelenmesi ve NiTiSn Biyomedikal Şekil Hafızalı Alaşımların Biyouyumluluğunun İyileştirilmesi

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Fizik Anabilim Dalı

Mayıs 2021, Sayfa: xiv + 104

NiTiSn şekil hatırlamalı alaşımlar, alaşım elementlerine, bileşimlerine, üretim tekniklerine ve diğer prosedürlere bağlı olarak çok yönlü uygulamalara sahiptir. Bu çalışma, birinci bölümde Ni_{50-x}Ti₅₀Sn_x ŞHA'lar, ikinci bölümde ise Ni₄₇Ti₅₀Sn₃ tel şeklinde alaşım olmak üzere iki bölümden oluşmuştur. Alaşımlar için diferansiyel taramalı kalorimetri, Vickers mikro sertliği, XRD, SEM ve EDX olmak üzere birçok farklı ölçüm yapılmıştır. Burada, alaşımların mikro sertliği ve kristalit boyutundaki değişimin uyum içinde olduğu belirlenmiştir. Martensit ve ostenit faz dönüşüm sıcaklıkları pik değerleri, DSC çevrim işleminin sayısı artırılarak daha düşük sıcaklığa taşınmış, ayrıca alaşımda Ni elementi yerine Sn elementi eklenerek faz dönüşüm sıcaklığındaki kayma hızı yükseltilmiştir.

İkinci bölümde, Tel şeklindeki NiTiSn ŞHA'larda TiO₂ kaplamanın etkisi ve biyouyumluk özelliklerinin iyileştirmeler incelenmiştir. Oksitlenmemiş ve oksitlenmiş NiTiSn-tel ŞHA'ların oksidasyon davranışları, faz dönüşümü sıcaklığı, kristal yapıları, mikro yapıları ve korrozivite değerleri açısından incelenmiştir. Ayrıca, Oksitlenmemiş ve oksitlenmiş tel için in vitro çalışması vücut sıcaklığında simüle edilmiş vücut sıvısı ve fizyolojik serumda gerçekleştirilmiştir. Oksitlenmemiş ŞHA'nın korozyon hızı simüle edilmiş vücut sıvısı ve fizyolojik serumda sırasıyla 481 ve 786 µm / yıl olarak bulundu ve bu, eşit atomlu NiTi ŞHA'lar için bildirilen değerden daha düşüktür. Sonuç olarak, NiTiSn-telinin oldukça biyouyumlu olduğu ve insan vücuduna implantasyon gibi çeşitli amaçlarla kullanılabileceği söylenebilir.

Anahtar Kelimeler: Düşük Sıcaklıklı Şekil Hatırlamalı Alaşım, NiTiSn, TiO₂, Faz dönüşümü, Kaplama, Biyouyumluluk, Korozyon

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SYMBOLS AND ABBREVIATIONS

Symbols

A_s	: Austenite start temperature
A_p	: Austenite peak
A_f	: Austenite finish temperature
M_s	: Martensitic start temperature
M_p	: Martensitic peak
M_f	: Martensite finish temperature
M^t	: Twinned martensite
M^d	: Detwinned martensite
A_s^t	: Austenite start temperature for $M^t \rightarrow A$ phase transformation
A_f^t	: Austenite finish temperature for $M^t \rightarrow A$ phase transformation
A_s^d	: Austenite start temperature for $M^d \rightarrow A$ phase transformation
A_f^d	: Austenite finish temperature for $M^d \rightarrow A$ phase transformation
M_s^d	: Martensite start temperature for $A \rightarrow M^d$ phase transformation
M_f^d	: Martensite finish temperature for $A \rightarrow M^d$ phase transformation
σ_s	: Stress start (for starting phase transformation)
σ_f	: Stress finish (for completing phase transformation)
C^A	: Austenite slope in stress-temperature phase diagram for martensite to austenite Phase transformation
C^M	: Martensite slope in stress-temperature phase diagram for austenite to martensite Phase transformation
e_v/a	: Valence electron concentration
c_v	: Valence electron
ΔH	: Enthalpy
ΔS	: Entropy
ΔG	: Gibbs free energy
G_e	: Elastic energy
D	: Crystallite size
λ	: Wavelength
K	: Scherrer constant
k_α	: Atomics emission spectra from L shell to K shell
$[uvw]$	: Miller indexes of direction
(uvw)	: Miller indexes of a plane

Abbreviations

<i>A</i>	: Austenite phase
<i>M</i>	: Martensite phase
<i>T</i>	: Temperature
SMA	: Shape Memory Alloy
SME	: Shape Memory Effect
HTSMAs	: High Temperature Shape Memory Alloy
SE	: Superelasticity
PE	: Psueelasticity
DSC	: Diffraction Scanning Calorimetry
XRD	: X-ray Diffraction
EDX	: Energy Dispersive X-ray
EDS	: Energy Dispersive X-ray Spectroscopy
SEM	: Scanning Electron Microscope
at. %	: Atomic percentage
wt.%	: Weight percentage
Ni	: Nickel
Ti	: Titanium
Sn	: Tin
O	: Oxygen
NiTi	: Nickel-Titanium
TiO ₂	: Titanium di-oxide
R-phase	: Intermediate phase
NiTiSn	: Nickel-Titanium-Tin
NiTiNOL	: Nickel-Titanium-Naval Ordnance Laboratory
MPa	: Mega Pascal
SIM	: Stress induced martensitic
ER	: Electrical resistivity
FWHM (B)	: Full width at half maximum
BT	: Body Temperature
RT	: Room Temperature
TT	: Transformation temperature
H	: Heusler
HH	: Half-Heusler

1. INTRODUCTION

Advances in technology today are based on improving the properties of materials with customized properties and high stability. Also, materials with definite functionalities that can self-adaptation to the environmental condition have received much attention. Shape Memory Alloys (SMAs) are one of the best choices for engineers among smart materials because of the novel features that give them a certain position. Pseudoelasticity (PS) and shape memory effect (SME) are two of the shape memory characteristic of SMAs that can return a deflected shape to the original morph by different mechanisms [1-5]. However, there are still some physical properties, such as thermal and mechanical stability, that need to be further developed. It has been reported that the SMAs' properties can be monitored by using three main parameters, including compositional rate [6], alloying by new elements [7-9], and the manufacturing techniques [10].

The first family of SMAs, which adopt in versatile application fields, was the equiatomic-NiTi SMAs found by Buehler and Wang [11]. The biomedical applications are the most contribution of NiTi-based alloys [12, 13]. It is worth highlighting some superior of SMAs for medical applications, including SME, PE, proper Young's modulus, and high corrosion resistance [14-16]. Researchers want to investigate Ti-based alloys for implantation with improved lifetime, higher corrosion resistance, costume mechanical properties, and good workability in the subject environment. Ti has been shown to be a biomaterial material that is passive in the human body [17].

Nowadays, SMAs have been used for making smart actuators in different areas. Options are NiTi-based SMAs that can generate a great output force through long distance shape recovery [18]. In the workplace, these actuators experienced many DSC cycling between two solid phases with different crystal structures (austenite phase (parent) $\leftrightarrow$ martensite phase), which reduce the performance of the alloy. For example, phase transformation temperatures (TTs) are shifted all through DSC cycling because a high-density of dislocations can be generated [19, 20]. Physical metallurgy is a method of manufacturing an alloy used to reduce dislocations and achieve good thermal stability [21, 22].

Many researches have been conducted for producing NiTi-based high-temperature shape memory alloys by alloying with new elements for non-medical applications [23, 24], however, studies on lower temperature shape memory alloys have limitations [8, 25, 26]. It should be kept in mind that adding a new element to an SMA influence all characteristics of the alloy, which makes it a little more complicated to control all parameters. Several parameters determined the substituting of the doped element instead of Ni or Ti in a NiTi SMA, including atomic size, valency, and electronegativity of the doped element [27]. Many researches have been conducted on the alloying NiTi alloy [28-30], which have revealed that some elements such as Sn [31, 32], Fe [25], Co [33], and Cr [34] reduce the TTs to lower temperatures.

The shape memory characteristics of Ni-Ti-Sn SMA was firstly found by Zheng et al. [35] in 2004 and then other researchers, such as Choi [36], Choe [32], Kim [31], and Tong [37] developed this alloy. Various physical properties of NiTiSn alloy can be changed, e.g., the phase transformation temperatures can be increased by substituting Ni with Sn element [31], while its fracture strain diminished from 7.6 to 3.5 % by changing Sn from 5 at.% to 12.5 at.% [38].

Metals are normally liable to corrosion and it is recognized that chloride solutions are listed as the most aggressive environments for metals. Corrosion is one of the disadvantages of metals when implanted in a tissue, which makes a restriction in the metallic surgical implantation, therefore in this field, only a selective number of the high corrosion-resistant alloys is utilized [39].

The impact of medical drugs having fluoride ions exhibits a particular issue for NiTi-based materials in dentistry [40]. Ti incorporated amorphous carbon nitride films can be deposited with a direct current magnetron sputtering technique. It has been found that the corrosion resistance of a-CNx films enhances with the Ti incorporation, likewise, it developed the corrosion potential and diminished the corrosion current density, consequently, the biocompatibility increases [41]. The corrosion resistance, of the Ti-based alloy (Ti-23Nb-0.7Ta-2Zr-1.2O) in a simulated body fluid (SBF) and an in-vitro cell response, was studied. It is found that all electrochemical and corrosion parameters have a comparably favorable value, showing nobler features, and notably, insignificant toxicity compared to the commercially pure Ti [42].

Parallel to stainless steel alloys, the nearly equiatomic NiTi SMAs are considered as good biomaterials candidates for implantation. Fadlallah et al. studied the dynamics response of the electrochemical behavior of NiTi in a simulated oral environment. They reported that the corrosion resistance of NiTi was sharply increased by the EGCG from $129 \text{ k}\Omega \text{ cm}^2$ to $1.10 \text{ T}\Omega \text{ cm}^2$, while pure titanium was increased slowly from $9.4 \text{ k}\Omega \text{ cm}^2$ to $11.3 \text{ k}\Omega \text{ cm}^2$ for the particular time 310 K. Also, they found that NiTi alloy has higher antibacterial performance compared with pure Ti [16].

Al-Mayouf et al. studied the influence of fluoride ion concentration and pH value on the corrosion response of $\text{Ti}_{60}\text{Cu}_{30}\text{Ag}_{10}$ (wt.%) alloy. Their study was carried out using electrochemical techniques in artificial saliva solutions. They declared that the pH value and the concentration of fluoride ion can affect the corrosion behavior of the alloy, also the existence of Cu and Ag in the alloy has a positive effect on its corrosion behavior, particularly in acidic fluoride media [43].

NiTi alloy is primarily disposed to restricted corrosion when exposed to chloride solution, whereas it is susceptible to general corrosion in the fluoride solution [44]. To suppress the toxic impacts of titanium and nickel in living tissue, Yeung and coworkers modified the surface of NiTi alloy with a thin layer of TiN using a nitrogen plasma immersion ion implantation. The corrosion resistance of the implanted sample was improved compared to the original NiTi alloy and the stainless steel [45].

Nogueira and colleagues studied the corrosion behavior and electrochemical properties of Ti-Nb-Zr alloy in PBS solution with and without oxygen treatment. They stated that the corrosion resistance of the alloy was improved after the oxygen load. A stable titanium oxide layer on the surface of the alloy was produced that increased the corrosion resistance [46].

Ti-rich and equiatomic-NiTi SMAs have been acquired high passivation in an aggressive environment by coating their surfaces with an oxide film [47]. Leng and coworkers [48] stated that a titanium oxide film showed better compatibility in endothelial cells compared with pure titanium or a stainless steel alloy. A significant technique for surface modification is making an oxide layer on the surface of the implanted substance to make a protect tissue from the leakage of the constituents of the implant and endoscopic use. The surface can be treated through an oxidation process at high temperatures [49, 50]. Liu et al. coated a NiTi surface with a thin layer of TiO_2 , and they reported that the alloy showed better compatibility in the blood medium [51].

Kim et al. [38] stated that TTs decreased for substituting nickel with tin in NiTiSn alloy, and the shape recovery of the alloy was improved by the training process. They also found that the increase of the tin element in the alloy was responsible to develop the R-phase in the forward phase transformation process [38]. Due to some differences, such as atomic size, the solubility of Sn in NiTi alloy is limited, therefore it can impact the phase transformation of the alloy. Even though much researches have been conducted on the thermal, mechanical, and structural characteristics of Ni-Ti-Sn alloys [37, 38, 52, 53], the thermal stability, oxidation behavior, and biocompatibility in a simulated body fluid and physiological solution have not been investigated in in-vitro or in-vivo.

This study aims to investigate the biocompatibility of NiTiSn SMA by changing different parameters. It consists of two stages, firstly the alloy was made using the arc-melting technique with different compositions, and then a particular composition was selected to manufacture a wire-shaped alloy. All specimens were measured with the aid of differential scanning calorimetric to confirm shape memory behavior. Then other characteristic measurements such as X-ray diffraction and scanning electron microscopy were accomplished. The NiTiSn-wire SMA was subjected to high temperatures to make an oxide layer and then their biocompatibility was investigated by an in-vitro study. This dissertation is organized such that in the second chapter we introduced shape memory alloys, and their characteristics are clarified with corresponding sketches and diagrams. In the third chapter, a literature review was done for NiTiSn SMAs. In chapter four, different components and working principles of some instruments were clarified. The materials and the experimental procedure have been explained in chapter five. Chapter six includes the results and discussion of the study and finally, all outcomes of the study have been summarized in the conclusion chapter (chapter seven).

2. SHAPE MEMORY ALLOY AND MARTENSITIC TRANSFORMATION

In this chapter, shape memory alloys and their martensitic phase transformation have been described. Also, some tables and schematic diagrams are provided to clarify the subject.

2.1. Shape Memory Alloys

There are only 118 atoms that have been discovered, whereby some atoms can only be obtained in some special experiments and some of them are known as rare elements in the earth. On the other hand, most of the elements in the periodic table (Table 2.1) have been utilized by human beings. Each of the elements has its own physical and chemical characteristics, which make them unique. Depending on the features that they have, they are used in different areas, while their properties have been limited, thus it was necessary to improve them with several techniques. One of the effective techniques is doping pure materials with other elements. The new material (alloy) has different properties, which can be controlled by determining the amount of doped element. It should be noted that no chemical reactions occur between the components of the alloy and the elements share only their physical properties. In nowadays technology, alloy materials have occupied a wider range in most applications compared to pure materials. There are plenty of examples such as bronze, steel, and cast iron that influenced civilizations.

2.2. Phase Diagram

Most of the physical characteristics of materials are affected by some parameters, including temperature, pressure, and composition of their constituents. Therefore, the phase diagram of materials has received great attention among material scientists. A phase diagram can be demonstrated in two or three dimensions, in which each axis can represent a physical parameter. In metallurgy, phase diagrams are normally exhibited between the temperature and composition of constituents. The different phases are separated by a line that normally consists of solid and liquid phases.

Figure 2.1 shows the phase diagram of Ni-Ti alloy, where the y-axis and x-axis represent absolute temperature (in kelvin) and composition of nickel constituent, respectively. It should be noticed that since the composition is in atomic percentage (at. %), then by increasing Ni (from left to right) the composition of titanium decreased. In addition, there are some particular temperatures, including eutectoid and eutectic temperatures, that a phase completely transferred. The alloy can transfer from solid to the liquid state by absorbing an amount of heat (the latent heat of fusion) when its temperature increased to eutectic temperature. Conventionally, the left and right

Table 2.1. Periodic table.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1	1 H Hydrogen					Metals					Non-Metals							2 He Helium		
2	3 Li Lithium	4 Be Beryllium				Alkali metal	Alkaline earth metal	Lanthanide	Actinide	Post-transition metal	Metalloid	other non-materials	Noble gas		5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
3	11 Na Sodium	12 Mg Magnesium						Actinide												
4	19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton		
5	37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon		
6	55 Cs Cesium	56 Ba Barium		72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon		
7	87 Fr Francium	88 Ra Radium		104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessee	118 Og Oganesson		
				57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Europium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium		
				89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium		

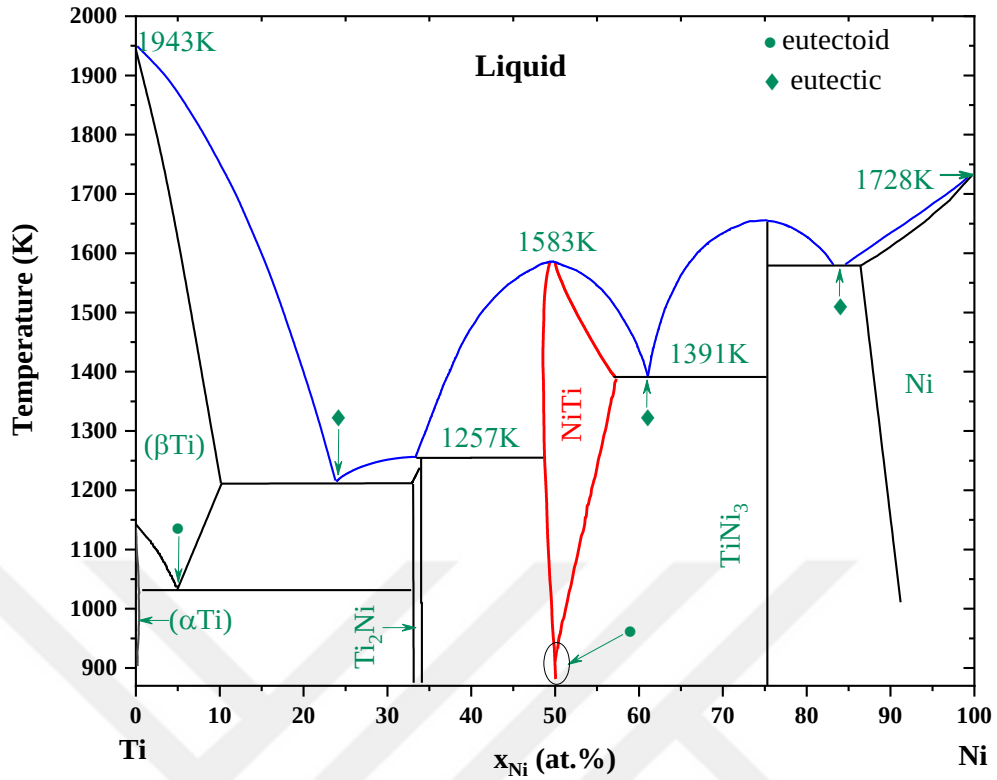


Figure 2.1. The binary Ni-Ti phase diagram (reprinted), adapted from [6].

sides of eutectic temperature are called pre-eutectic and hypo-eutectic temperatures, respectively. Another important temperature is eutectoid temperature, where the material transforms from a particular crystal structure to a different one. Likewise, the left and right-hand side of the eutectoid have the same name with a prefix of pre and hypo terms, respectively.

The eutectoid point is one of the key points for SMAs. There is a specific range of composition that an alloy may show shape memory characteristics. Figure 2.1 illustrates a red-colored area with austenite-B2 phase and is the key phase for a nitinol (NiTi SMA) to show shape memory feature. There is also another eutectoid that Ti composition is rich. Usually, based on the different constituents, an SMA may show a different phase diagram with one or more eutectoid points.

2.3. Martensitic Phase Transformation

An SMA has an austenite phase in the higher temperature and martensite phase in the lower temperature regions. Normally, since a predetermined shape of SMAs is given in the austenite phase, so austenite sometimes is called the parent phase, and the martensite is called the product. Austenite has a high ordered phase, while martensite can be appeared in either twinned or

detwinned form. Although phase transformation is a diffusionless transformation, the different crystal structure is given various physical properties.

In liquid-solid or solid-liquid phase transformation, normally there is a single temperature of the phase transformation. Unlike, in the solid-solid phase transformation, there are four characteristic phase transformation temperatures. In an SMA, the austenite phase begins to transform to the martensite phase at M_s (martensite starts temperature). However, the transformation continued by decreasing the temperature and in a specific temperature, M_f (martensite finish temperature), the transformation stops. On the other hand, when the SMA is heated, the martensite-austenite phase transformation starts at a different temperature, known as A_s (austenite start temperature) and the transformation continued for a range of temperature until it reaches A_f (austenite finish temperature). Additionally, the martensite phase can be formed above A_f under external stress, while this transformation is limited by a temperature, known as M_d (martensite deformation temperature) [54]. These characteristic temperatures are important and they are normally determined in most artificial SMAs. Also, based on these characteristic temperatures, the SMAs have been classified into high-temperature SMAs, such as NiTiHf [55] and NiTiZr [56], and low-temperature SMAs, such as binary-NiTi and NiTiSn [57]. In NiTi and NiTi-based SMAs, the transformation temperatures (TTs) strongly depend on the composition of constituents. Khalil-Allaf et al. [58] collected TTs for NiTi alloy for different Ni content, and they showed the dependency of TTs to Ni concentration.

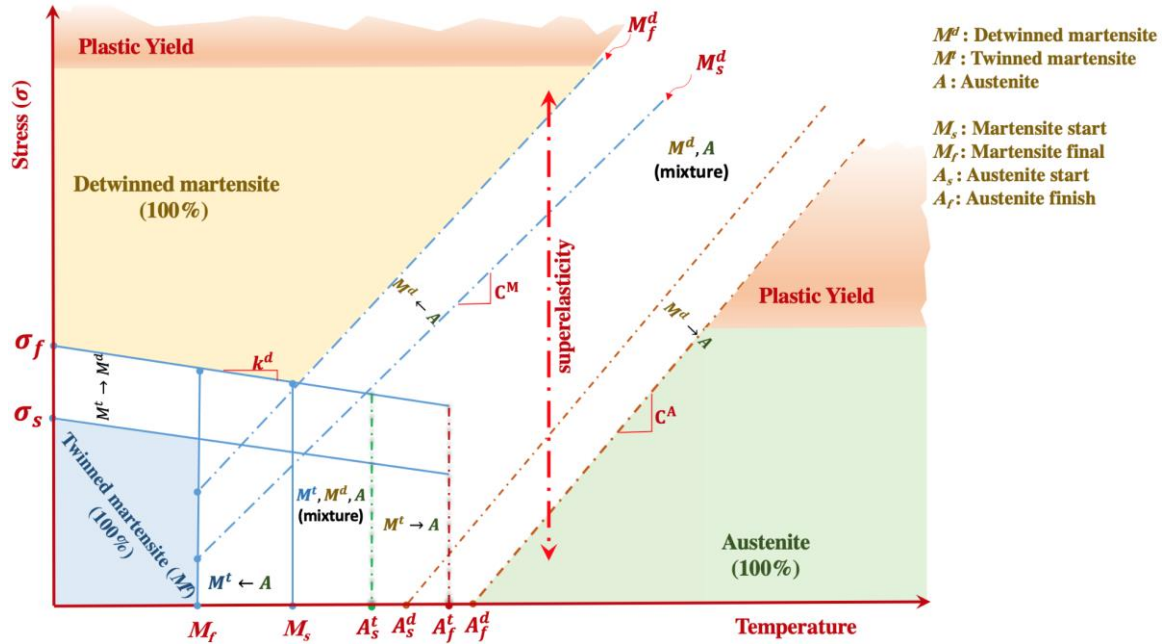


Figure 2.2. Schematic representation of stress-temperature phase diagram for an SMA, redraw and adapted from [59, 60]

Figure 2.2 displays a schematic diagram of stress-temperature for an SMA. Different scenarios can be considered for the phase transformation of an SMA. Only in some particular areas of the diagram, each austenite (A), twinned-martensite (M^t), and detwinned-martensite (M^d) can be found. A combination of A , M^t , and M^d can be detected in the intermediate phases. Superelasticity is shown as an isothermal process ($A \rightarrow M^d$) by increasing stress the austenite is transformed to M^d . Both M^d and A phases reach plastic yield by increasing stress. At zero stress, the transformation of $A \rightarrow M^t$ can occur. The diagram reveals different austenite start and austenite finish for martensite to austenite phase transformation. The austenite start and finish for $M^d \rightarrow A$ is higher than $M^t \rightarrow A$, because additional energy needs to be absorbed by the SMA to reverse the inelastic strain around the martensite-austenite interface. Also, the transformation for A to M^d phase in higher stresses need more nucleation energy so M_s^d and M_f^d is higher than M_s^t and M_f^t . The slopes of austenite $\leftrightarrow$ detwinned martensite are positive (C^A and C^M), while the transformation of $M^d \leftrightarrow M^t$ has a negative slope (k^d).

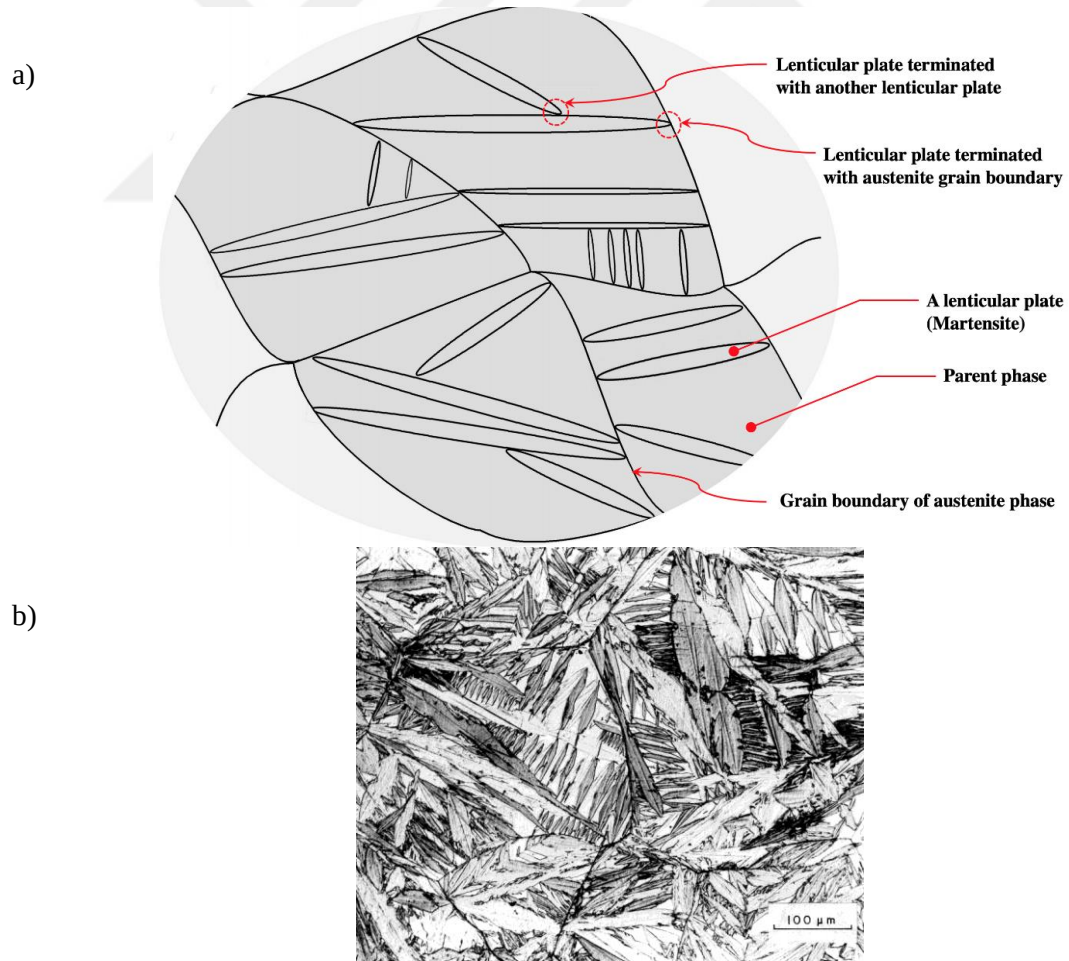


Figure 2.3. (a) The nucleated lenticular plates (martensite phase) inside austenite grains. The plates terminated with the austenite grain boundaries and/or with similar lenticular plates. (b) A particular SEM image of Fe-Ni-C alloy shows lenticular plates [61]

In NiTi-based SMAs, some phases can be detected depending on temperature, composition, manufacturing, and other treatments. For example, B2 can be detected for almost all NiTi-based SMAs in the high-temperature austenite phase. Also, B19' can be found in the low-temperature martensite phase. For binary NiTi SMAs, many studies reported an intermediate phase (R-phase) between B2 and B19', which is responsible for a two-step phase transformation process [62, 63].

Many lattice twins have been reported for B19' in the martensite phase of NiTi SMA. The major twin is $\langle 011 \rangle$ type II, which provides two martensite variants that have a relationship, i.e., they can be rotated 180° around their [011] direction [64]. The sheer lattice distortion (Bain distortion [65]) happens for the austenite phase during austenite $\rightarrow$ martensite phase transformation. This displacement is less than a lattice constant (interatomic distance). Two invariants distorted through Bain strain and rigid body rotation. Also, thin lenticular plates developed in austenite grains during martensite phase transformation. The growing martensite variant is around the velocity of sound for NiTi SMA for the temperature range of (-50 to 100 °C) [66], which provides a diffusionless process. The interface between austenite-martensite phases moves through the austenite phase transformation that belongs to the glissile interface. Glissile interface is a specific feature of SMAs to have a thermo-elastic reversible phase transformation (an ordinary material obeys sessile interface through a diffusion process) [60]. Similar to the other microstructures, initially the martensite plates are thin, and then they can grow up and make thick plates, however, their size is limited by the boundaries of the parent grain. Figure 2.3 shows lenticular plates growing in the parent phase and terminated with the austenite phase boundary and/or with the other lenticular martensite plates. The producing plates are an autocatalytic reaction such that when a single plate is nucleated it works as an electrolyte for producing the same plates [66].

In SMA, there are two important properties, which are shape memory effect (SME) and pseudoelasticity (or superelasticity).

2.4. Shape memory effect and Superelasticity

Martensite phase forms typically with a change of crystal structure, however, the martensite volume stays constant, and thus due to this accommodation, a strain is developed between the martensite phase and the matrix phase. For an elastic strain, the martensite-matrix boundary can move without difficulty throughout a reversible process. Temperature is the key point for transformation between parent and accommodated martensite phase, i.e., By heating, martensite platelets shrink, and by cooling the martensite phase is formed.

The shape memory effect (SME) is the SMA capability that can be achieved for alloys containing both martensite and austenite phases [67]. Figure 2.4 shows the schematic diagram of the atomic arrangement in shape memory and ordinary crystalline alloy. An SMA has SME and

superelasticity (SE) that help it to memorize its pre-determined shape. The SMA is manufactured at temperatures above austenite finish (A_f), and thus, it takes the first shape. The bases (atoms or compounds) arrange in a cubical lattice with high similarity. When the SMA is cooled to below martensite finish temperature (M_f), the crystal transformed to a new rearrangement, which manifests in a zigzag pattern. The atomic arrangement in the martensite phase is called twinning. On the other hand, an ordinary material may show more than one crystal structure in a solid phase, however, the twinning crystal structure is the specific phase of the SMAs. The twinned martensite is detwinned by an external load. After the external load is removed a deformation occurs. The detwinned crystal structure can be back to the parent phase, so the temporary deformation can be treated. Unlikely, an ordinary material can transform to higher temperature phases, but it cannot recover its pre-determined shape, therefore lattice-twin is an essential property for a crystalline material to reveal SME [68]. The reversible phase transformation in SMAs is a first-order, diffusionless solid-solid transformation [60], and also, it is a type of thermo-elastic transformations [69].

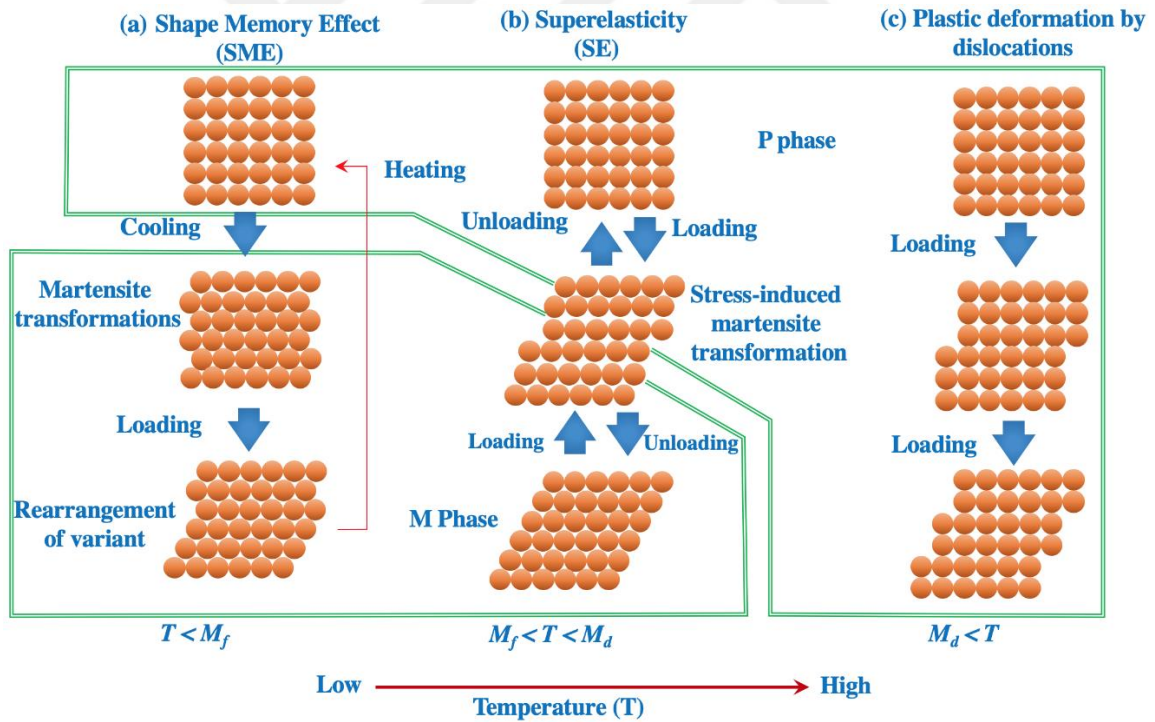


Figure 2.4. Schematic diagram of atomic arrangement in crystalline material for the shape memory effect and (b) superelasticity of an SMA, and (c) plastic deformation by dislocations of an ordinary material [70]

Figure 2.5 displays a three-dimensional schematic diagram for an SMA that shows SME and SE. Both stress and temperature have affected the phase and crystal structure. When an SMA with a martensite phase is loaded, it shows elastic behavior like other ordinary materials. If the load is

removed the absorbed elastic energy works as a restoring force and treats the distortion of the crystal structure. For particular stress, the alloy deforms, which means the appearance of the alloy is changed. An external force can make slip between atomic lattice planes, and thus, the material is permanently deformed. This property describes as plastic deformation. The higher the plastic deformation, the more ductility the material.

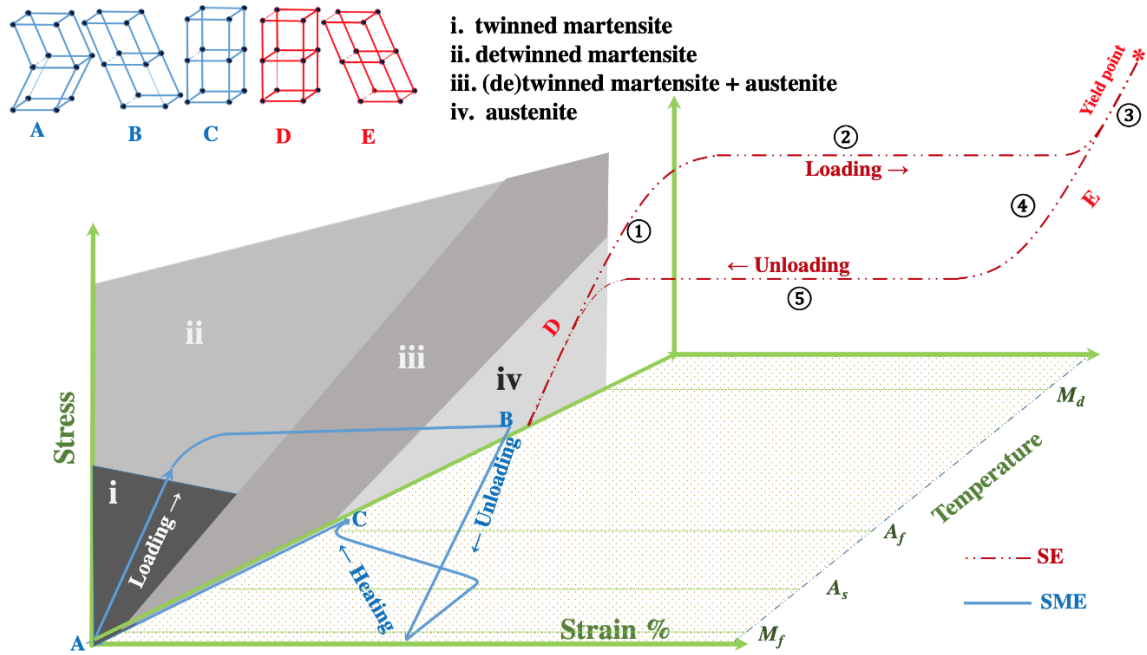


Figure 2.5. Schematic representations of superelasticity and shape memory effect of SMA

The deformation in an ordinary material is happened by introducing slips, where the lattice planes displaced and make a permanent deformation (Figure 2.6a). An SMA may experience the same deformation, while their atoms change arrangements such that the twinning martensite transformed into detwinned martensite, thus the predetermined shape is memorized in the alloy (Figure 2.6b). The deformed SMA should be heated to the austenite phase to restore the induced strain. During these transformations, the detwinned martensite changes its phase to the austenite phase, so the material can recover its original shape. This phenomenon is called the shape memory effect.

Another superior feature of a shape memory material is superelasticity (SE), but since the process is not perfectly elastic, so pseudoelasticity is used instead. Figure 2.5 reveals SE, which an isothermal process. This property is restricted for a temperature range between A_f (austenite finish temperature) and M_d (martensite deformation temperature). Initially, the alloy experience an elastic deformation, which its modulus depends on the composition of the alloy. Figure 2.7 displays the stress-strain behavior of NiTi SMA and some other bio-materials used for implantations. In the second stage, a transformation is taken place from the austenite phase to an unstable martensite

phase. For a NiTi SMA, Chowdhury et al. [71] showed how the austenite-B2 phase transforms to B19' under applied stress. When further stress is applied to the unstable martensite, it can show a new elastic behavior, however, the alloy may undergo slip and finally fracture as the external force increases. An SMA can recover strain, which depends on the type of alloy [72], the magnitude of the applied force [73], and the number of mechanical cycles [74].

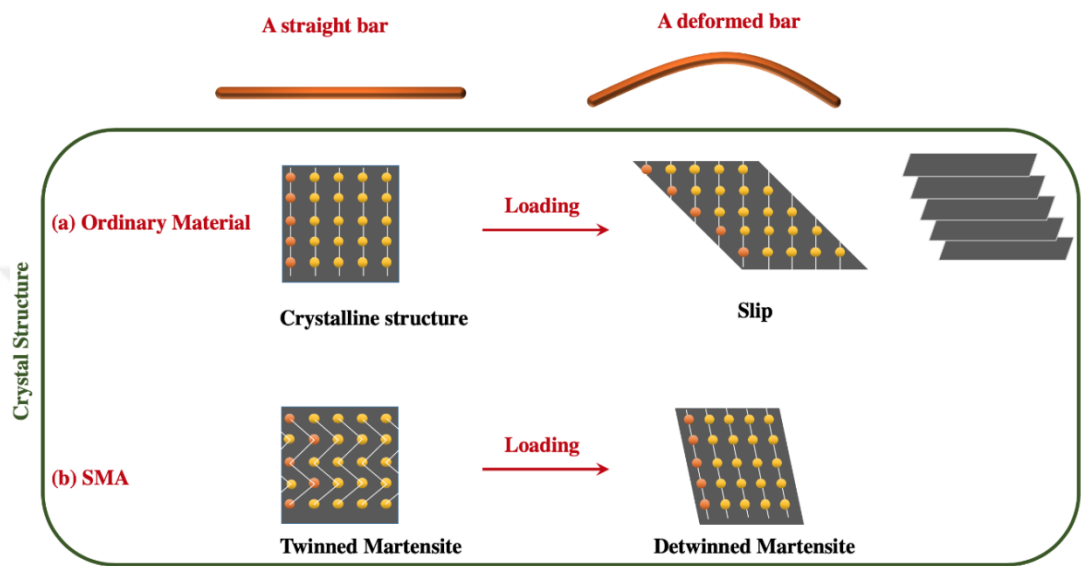


Figure 2.6. Schematic representation of distortion of an (a) SMA and slip in (b) an ordinary material under an external force

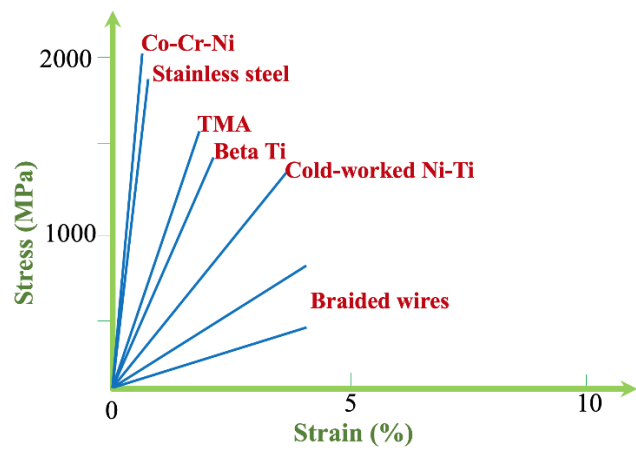


Figure 2.7. The stress-strain behavior of NiTi alloy with some bio-materials [5, 15]

3. NiTiSn SHAPE MEMORY ALLOYS

This chapter describes the crystal structure and some properties of each component and constituent in NiTiSn alloy.

3.1. Nickel, Titanium, and Tin

Nickel (Ni) is a transition metal with 28 protons, and a pure ingot has a white-silver color. It has a face centered cubic (FCC) crystal structure. Figure 3.1 reveals the nickel crystal structure. Although Ni can react with oxygen at room temperature, after producing a thin layer of Ni-oxide on the surface, the Ni converts to a passive material. Thus, Ni can be classified as a corrosion-resistant material. Similar to iron (Fe), Ni is a ferromagnetic element that loses this ability above the curie temperature of 358 °C [75].

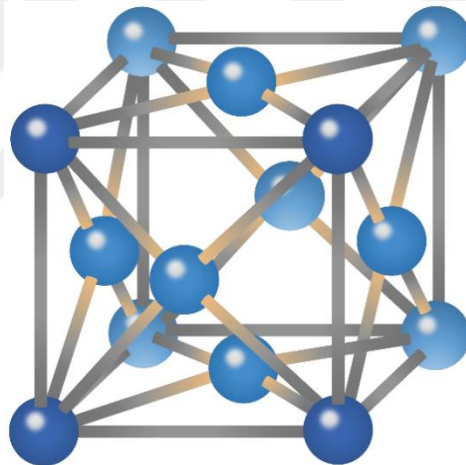


Figure 3.1. Nickel crystal structure (FCC)

Ni is comparably cheap and has many unique properties, which grows its applications in terms of alloys. One of the prompted extended alloys is nitinol that an equilibrium atomic percent of nickel and titanium gives a shape memory characteristic to the alloy. That is why it has been used for implant purposes [10]. However, it is reported that Ni shows carcinogenicity, so its toxicity and other side effects should be taken into account especially for implant applications [76].

Titanium (Ti) has two crystal structures, which depend on the temperature. In high-temperature Ti shows body-centered cubic (BCC) or β –crystal structure and in low temperature, it reveals hexagonal close-packed (HCP) or α –crystal structure (Figure 3.2) [77]. Normally, the temperature of 1155.6 K is reported as the transformation temperature between α and β phases, while its can triggered by alloying with other elements such as Ni, which is displayed in the Ni-Ti

phase diagram (Figure 2.1). It has been found that some elements increase the stability of these phases; for example, lightweight elements such as Al, O, N, and C as known as α –stabilizers; on the other hand, some elements such as Mo, V, Ta, and Nb increase β –isomorphous stability; whereas, Fe, Ni, Mn, Cu, Co, Si, and H increase β –eutectoid stability. Both β –isomorphous and β –eutectoid elements are known as β –stabilizers [78]. β –phase has higher biocompatibility compared to α –phase, since its Young modulus value is closer to bone.

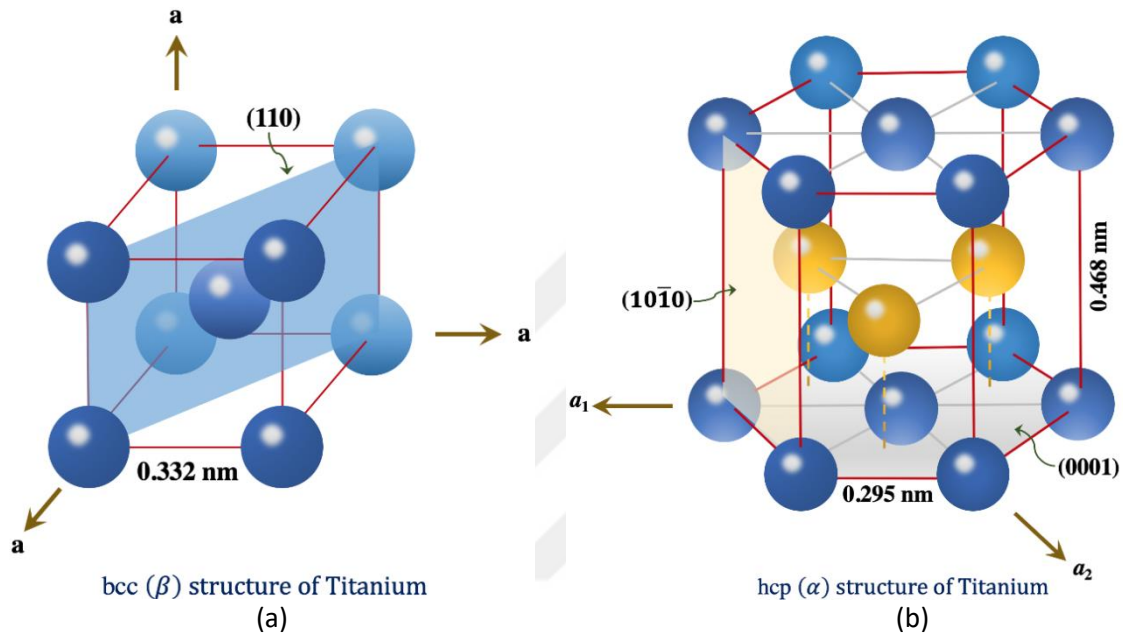


Figure 3.2. Titanium crystal structure. (a) at high temperature has a bcc crystal structure and (b) in low temperature has hcp crystal structure. The colors are only to represent the position of atoms

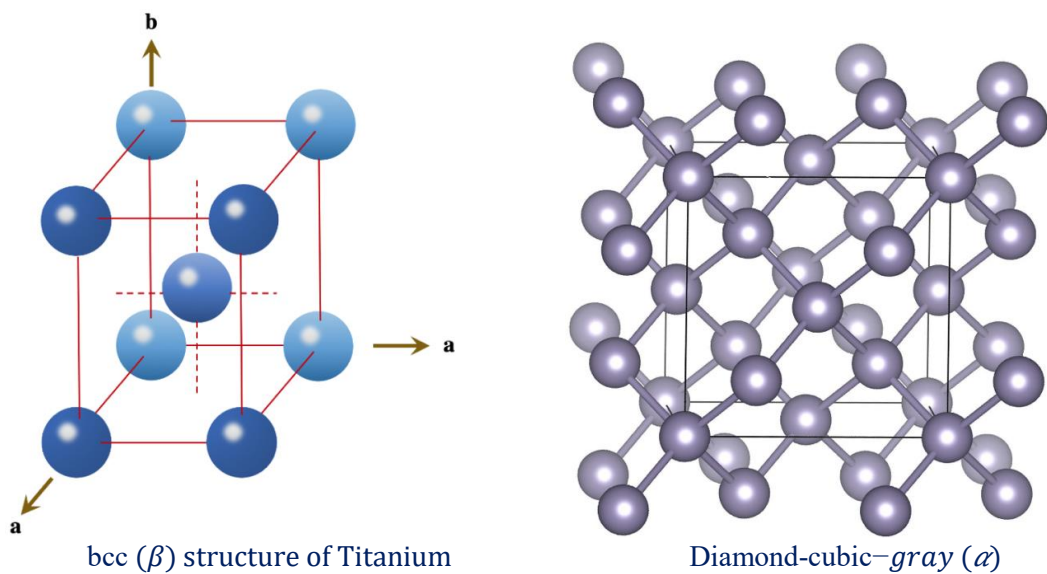


Figure 3.3. Tin (Sn) crystal structures

Table 3.1. A summary of the biological behavior of some elements, where red, yellow, and green represent a serious, moderate, and minimal/no concern, respectively [79-116]

Periodic position	Element	Biocompatible	Carcinogenic	Genotoxic	Mutagenic	Cytotoxic	Allergenic	Pron to corrosion	Other
3d	Ti	Yes	No	No	No	Med	No	No	No
	V	No	Yes	Yes	Yes	High	Disputed	No	No
	Cr	No	Disputed	Yes	Yes	High	Yes	No	No
	Mn	No	No	Yes	No	High	No	Yes	No
	Fe	No	No	Yes	No	Med	No	Yes	No
	Co	No	Yes	Yes	Yes	High	Yes	Yes	Yes
	Ni	No	Yes	Yes	Yes	High	Yes	Yes	Yes
	Cu	No	No	Yes	Yes	High	Yes	Yes	Yes
4d	Zr	Yes	No	No	No	Low	No	No	No
	Nb	Yes	No	No	No	Low	No	No	No
	Mo	No	Disputed	Yes	Yes	Low	Yes	Yes	Yes
	Tc	No	-radioactive-						
	Ru	No	No	No	No	Med	No	No	Yes
	Rh	No	Yes	Yes	Yes	High	Unknown	No	No
	Pd	No	Yes	No	Disputed	Med	Yes	No	No
	Ag	No	No	No	No	High	Yes	No	Yes
5d	Hf	Unknown	Unknown	Unknown	Unknown	Med	No	No	Unknown
	Ta	Yes	No	No	No	Low	No	No	No
	W	No	Yes	Yes	No	Med	No	Yes	No
	Re	Unknown	Unknown	Unknown	Unknown	Unknown	No	No	Unknown
	Os	No	Unknown	Yes	Yes	High	No	Yes	No
	Ir	No	No	No	Yes	High	No	No	Yes
	Pt	No	Yes	Yes	Yes	High	Yes	No	No
	Au	Yes	No	No	No	High	No	No	No
Other	Al	No	No	Yes	No	Low	No	No	Yes
	Zn	No	No	No	No	High	No	No	Yes
	Sn	Yes	No	No	No	Low	No	No	Yes

Tin (Sn) is a non-transition metal that has the electronic configuration [Ne]3s²3p [38]. Figure 3.3 reveals that tin has many allotropic forms such as white (β), with body-centered tetragonal crystal structure, and gray (α), which provides diamond cubic. It is reported that Sn is a low cytotoxic material with no prone to corrosion, which makes it be classified as a high biocompatible element [117].

The Ni element has a lower melting point compared to the titanium element. A pure Ni or Ti has no shape memory features, but together they can give this characteristic to a NiTi alloy. This can be classified as an emergence phenomenon. However, Ni is not a biocompatible material, so when NiTi alloy is used for implanting purposes, that organ has to be protected from Ni exposure. Titanium, on the other hand, has known as an expensive material that has comparably high biocompatibility. Likewise, tin is an inexpensive biocompatible element with sufficient biocompatibility. Table 3.1 reveals some basic information about the biological effects of some elements. Substituting Ni with Sn element in NiTi-based SMA can enhance the biocompatibility of the alloys. In addition, Ti can react with oxygen to make TiO₂ that can make a barrier for leakage of Ni elements into the human organs.

3.2. Corrosivity

Corrosivity and oxidation are two different terms explained in the present and the next sections. The corrosion can take place in a wet medium, where the substance and medium role as electrode and electrolyte. The atoms on the surface of the substance interact with the atoms that exist in the electrolyte, therefore, oxidation (oppositely a reduction that happened for the atoms in the electrolyte) happens for the substance. The electrochemical process is a fast and unexpansive technique to measure the corrosivity of a material. In this method, an electric current is applied throughout an electric circuit, including two electrodes (the sample and a counter), a power supply, an electrolyte, sensitive voltmeters, and ammeters.

Some factors can influence the rate of corrosion such as temperature, type of electrolyte, type of constituents [118], precipitation [119], heterogeneity, and residual stress [120]. Materials can prevent corrosion by controlling the design, cathodic protection, inhibitors, coating, and select sufficient materials for a particular application [118].

As an example, it can be said that the etching process, which is used for identifying grain boundaries of crystalline materials, is a corrosion process, where the acidic solution works as an electrolyte and the variation of the compositional ratio between the grains and the boundaries role as an active-passive concentration cell.

3.3. Oxidation

Oxidation is a general term used for losing electrons. The electron can be gained by oxygen, nitrogen, carbon, etc. In opposite to corrosion that has only disadvantages, oxidation has both disadvantages and benefits in a different situation. For example, a thin layer of TiO_2 on the surface of NiTi alloy can increase the biocompatibility of nitinol for medical purposes [51, 121].

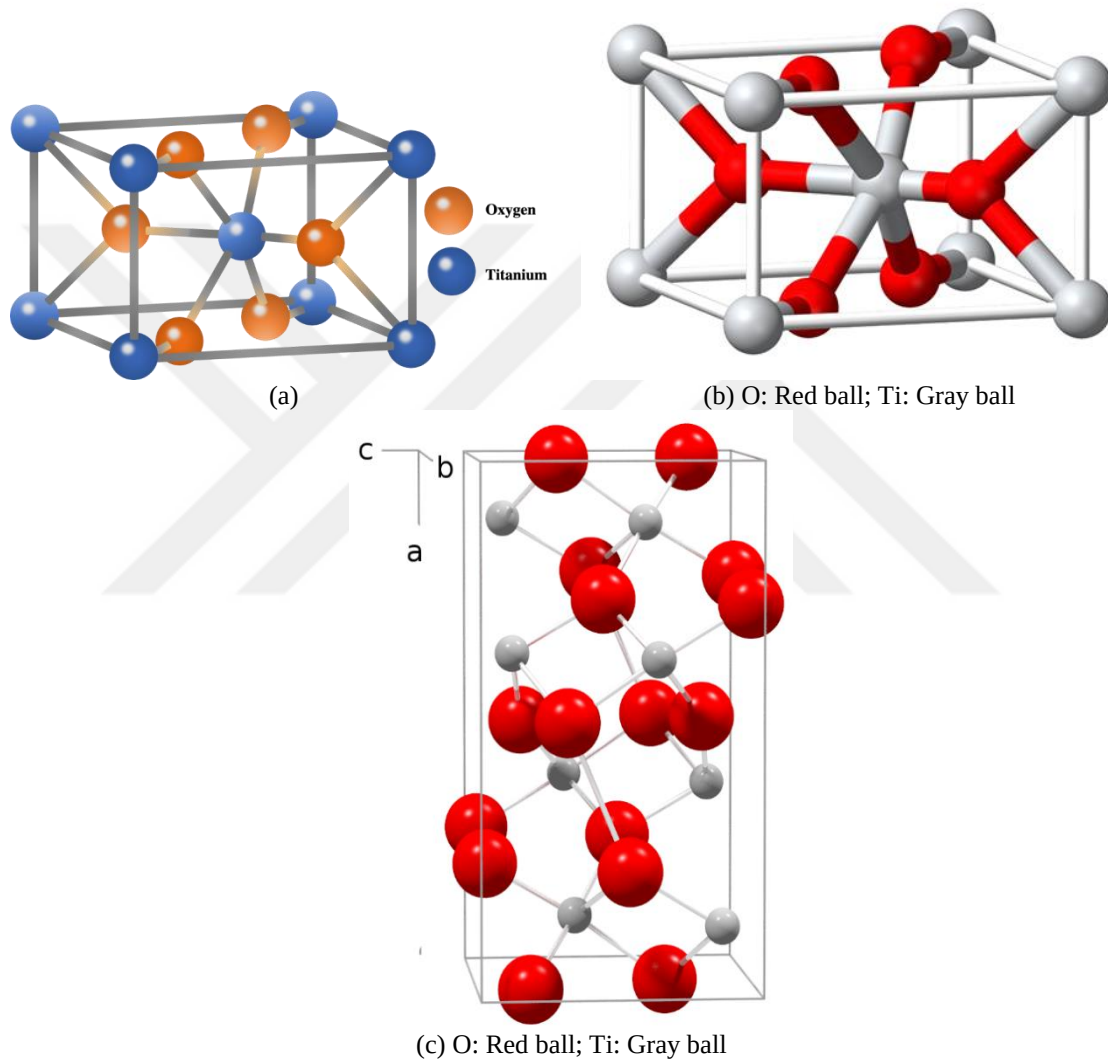


Figure 3.4. TiO_2 with three different crystal structures; (a) Rutile; (b) Anatase; (c) Brookite

3.3.1. Titanium Oxides

The type of metal oxide plays a crucial role to be specified as a biocompatible material because the oxide layer can control the corrosion process. Although some materials, such as Au and Pt are passive to oxidation, Ti, on the other hand, can interact with its environment and make different types of oxides. In a normal condition, an oxide layer can form in a fraction of a second

on the Ti material that can reach around 6 to 10 nm thick [122]. Additionally, Ti able to reform the oxide layer spontaneously whenever it is removed mechanically. The most stable type of Ti-oxide is titanium dioxide (TiO₂) with a high dielectric constant, also some other oxide compounds have been reported, such as TiO, Ti₂O₂, Ti₃O, Ti₃O₂, Ti₂O₃, and Ti₃O₅ [78]. The TiO₂ or titania is a compound that can be found with three different crystal structures, including, Rutile, Brookite, Anatase [123], and rarely Akaogiite [124]. Rutile is the most stable one. Figure 3.4 displays the three different crystal structures of TiO₂. Some crystal structural parameters are listed in Table 3.2.

Table 3.2. Some crystal structural parameters of TiO₂

	Space group	Crystal structure	Cell parameters (Å)	Density (g/cm ³)	Ref.
Rutile	<i>P4₂/mnm</i>	tetragonal	a =4.5936, c=2.9587	4.1	[125]
Anatase	<i>I4₁/amd</i>	tetragonal	a=3.784, c=9.51	3.79	[125]
Brookite	<i>Pbca</i>	orthorhombic	a=9.18, b=5.447, c=5.14	3.99	[125]
Akaogiite	<i>P2₁/c</i>	monoclinic	a=4.606, b=4.896, c=4.933	4.72	[124]

Table 3.3. The space group, enthalpy change of formation, and Gibbs free energy for the elements and compounds of Ni, Ti, and Sn [126]

Compound	Space group	Enthalpies of formation eV/atom	Gibbs free energy eV/atom
Ti	<i>P6₃/mmc</i>	—	—
Ni	<i>Fm$\bar{3}$m</i>	—	—
Sn	<i>I4₁/amd</i>	—	—
Ti ₆ Sn ₅	<i>P6₃/mmc</i>	-0.381	—
Ti ₅ Sn ₃	<i>P6₃/mmc</i>	-0.348	+0.005
Ti ₂ Sn	<i>P6₃/mmc</i>	-0.338	—
Ti ₃ Sn	<i>P6₃/mmc</i>	-0.301	—
Ti ₂ Ni	<i>Fd$\bar{3}$m</i>	-0.288	—
TiNi	<i>Pm$\bar{3}$m</i>	-0.411	—
TiNi ₃	<i>P6₃/mmc</i>	-0.478	—
Ni ₃ Sn	<i>P6₃/mmc</i>	-0.247	—
Ni ₃ Sn ₂	<i>Pnma</i>	-0.323	—
Ni ₃ Sn ₄	<i>C2/m</i>	-0.279	—
TiNiSn	<i>F$\bar{4}$3m</i>	-0.715	—
TiNi ₂ Sn	<i>Fm$\bar{3}$m</i>	-0.622	—
Ti ₂ Ni ₂ Sn	<i>P4₂/mnm</i>	-0.485	+0.109
Ti ₅ NiSn ₃	<i>P6₃/mcm</i>	-0.388	+0.076

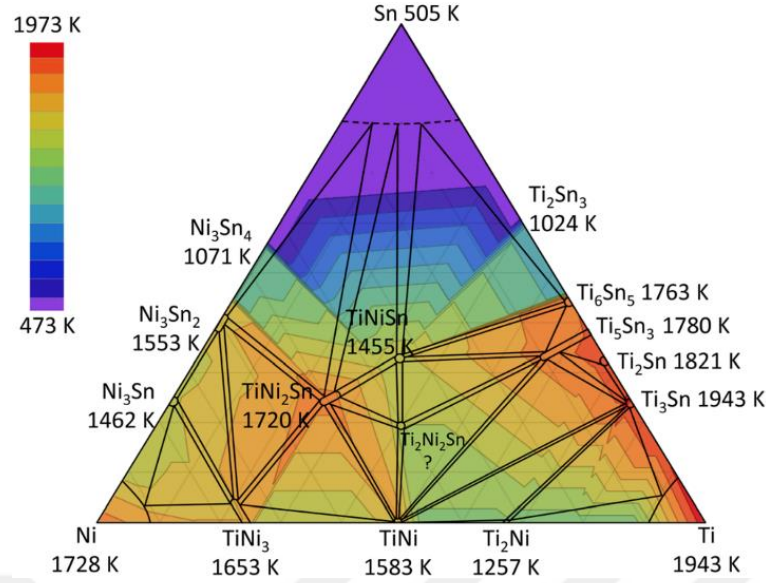


Figure 3.5. Triple phase diagram for NiTiSn alloy. The colors represent different melting point based on the composition [126]

3.4. NiTiSn Alloy

NiTiSn is a ternary alloy consists of Ni, Ti, and Sn elements. The alloy can show shape memory characteristics for a range of compositional rates. In the binary NiTi diagram (Figure 2.1), is was seen that the martensitic transformation could be achieved for only compositions around the equiatomic of Ni and Ti. Besides, the temperature of melting point T_m for the alloy strongly depends on the composition of constituents (Figure 3.5). For example, Ti-rich alloy has comparably high T_m , while Sn-rich alloy has a low T_m . In thermodynamics, each element has its own phase diagram and has some constant characteristics values that independent of its amount. While in an alloy, the constituent elements shared their properties, and the more the number of components, the higher the complexity and differences in compounds in the phase diagram of the alloy. Romaka et al. [127] determined different compounds in the Ni-Ti-Sn system as a function of composition. Some compounds are binary, including TiNi, Ti₂Ni, TiNi₃, Ti₃Sn, Ti₂Sn, Ti₅Sn₃, Ti₆Sn₅, Ni₃Sn, and Ni₃Sn₂, where the rare constituents dissolved in the dominant element phases. Also, there are some ternary compounds, such as TiNiSn (half-Heusler compound), Ti₅NiSn₃, TiNi₂Sn (full-Heusler compound), and Ti₂Ni₂Sn that can be found for some specific compositions. Each of the aforementioned compounds needs different formation energy. Table 3.3 lists the enthalpy change and some other thermodynamics and crystal structure of the compounds. The enthalpy change for the formation of compounds (ΔH_f) and the temperature-dependence-Gibbs free energy of compound ($G_c^{Ti_xNi_ySn_z}$) can be calculated by using the following formulas [126]:

$$\Delta H_f(Ti_xNi_ySn_z) = E_{Ti_xNi_ySn_z}^{min} - \frac{x E_{Ti_x}^{min} + y E_{Ni_y}^{min} + z E_{Sn_z}^{min}}{x + y + z} \quad (3.1)$$

$$G_c^{Ti_xNi_ySn_z}(T) = \dot{x}^0 G_{Ti}^{HCP} + \dot{y}^0 G_{Ni}^{FCC} + \dot{z}^0 G_{Sn}^{Sn} + A^{Ti_xNi_ySn_z} + B^{Ti_xNi_ySn_z} T \quad (3.2)$$

where the minimum total energy per atom for Ti, Ni, and Sn are represented by $E_{Ti_x}^{min}$, $E_{Ni_y}^{min}$, and $E_{Sn_z}^{min}$. Also, $\dot{x}$, $\dot{y}$, and $\dot{z}$ are the values of the normalized chemical formulae. Furthermore, G_{Ti}^{HCP} , G_{Ni}^{FCC} , and G_{Sn}^{Sn} are Gibbs free energy of Ti, Ni, and Sn in the ground state crystal structure, respectively. HCP, FCC, and Sn in the superscript of the Gibbs free energy of elemental compounds are the ground state structure. In Eq. (3.2), the enthalpy and entropy of compound formation are represented as A and B, which at absolute zero temperature (0 K), B can be negligible.

As a definition of alloy, it is known that different elements share their properties and make a new substance. However, it is different from a compound that is produced through a chemical reaction and making a bond. The constituents propagated inside the alloy homogeneously and they can occupy a site of a lattice or can role as an interstitial atom. Naturally, during producing an alloy, some compounds nucleated and growing that influence the properties of the alloy.

Figure 3.6 reveals Ni, Ti, Sn elements and the most probably compound produced in NiTiSn alloy. It can be seen that the energy of formation per atom is different for different compounds, thus the friction of them depends on the amount of energy absorbed by the alloy. Additionally, they have various densities, therefore they can have different mechanical properties, such as hardness. Also, the stability of each of them compared to the other compounds depends on the crystal structure.

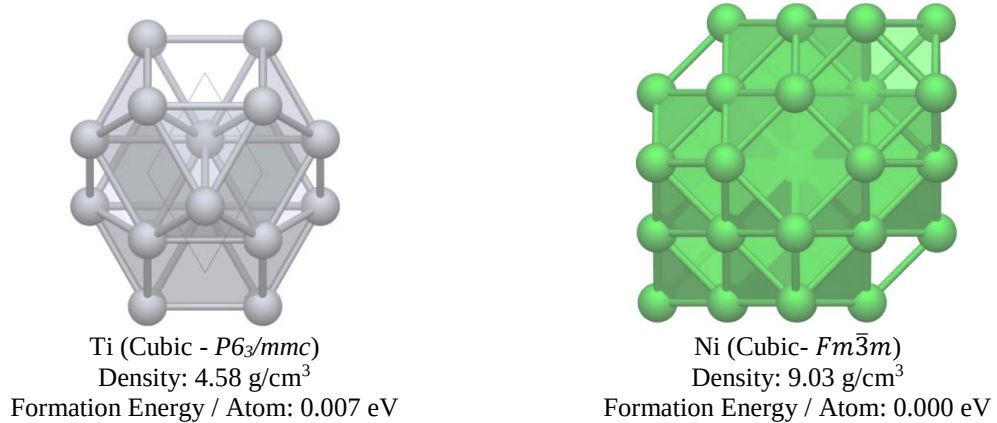


Figure 3.6. The crystal structure, density, and formation energy of all constituents and compounds that may be present in a NiTiSn alloy [128-138]

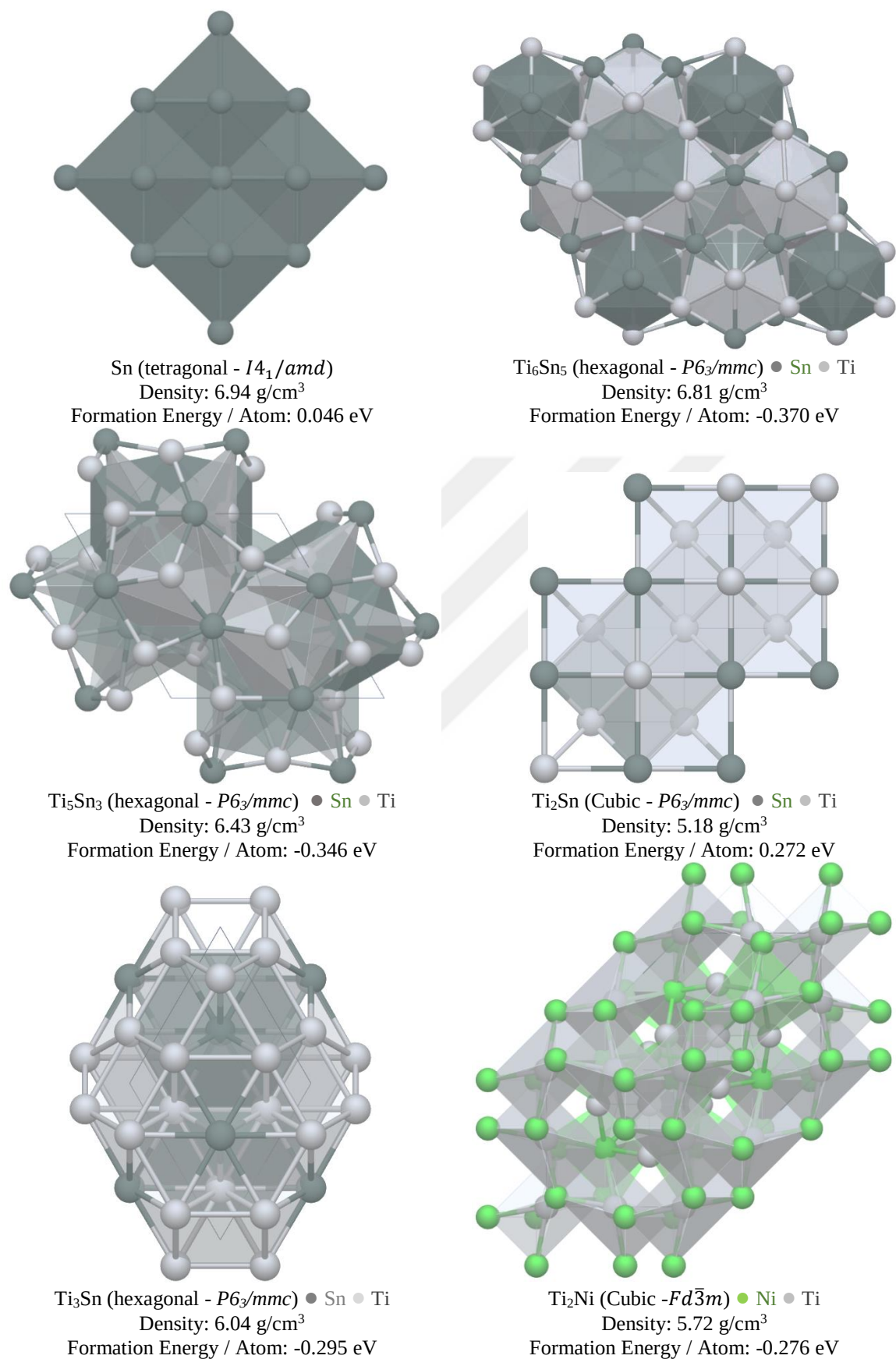


Figure 3.6. The crystal structure, density, and formation energy of all constituents and compounds that may be present in a NiTiSn alloy [128-138] (continue)

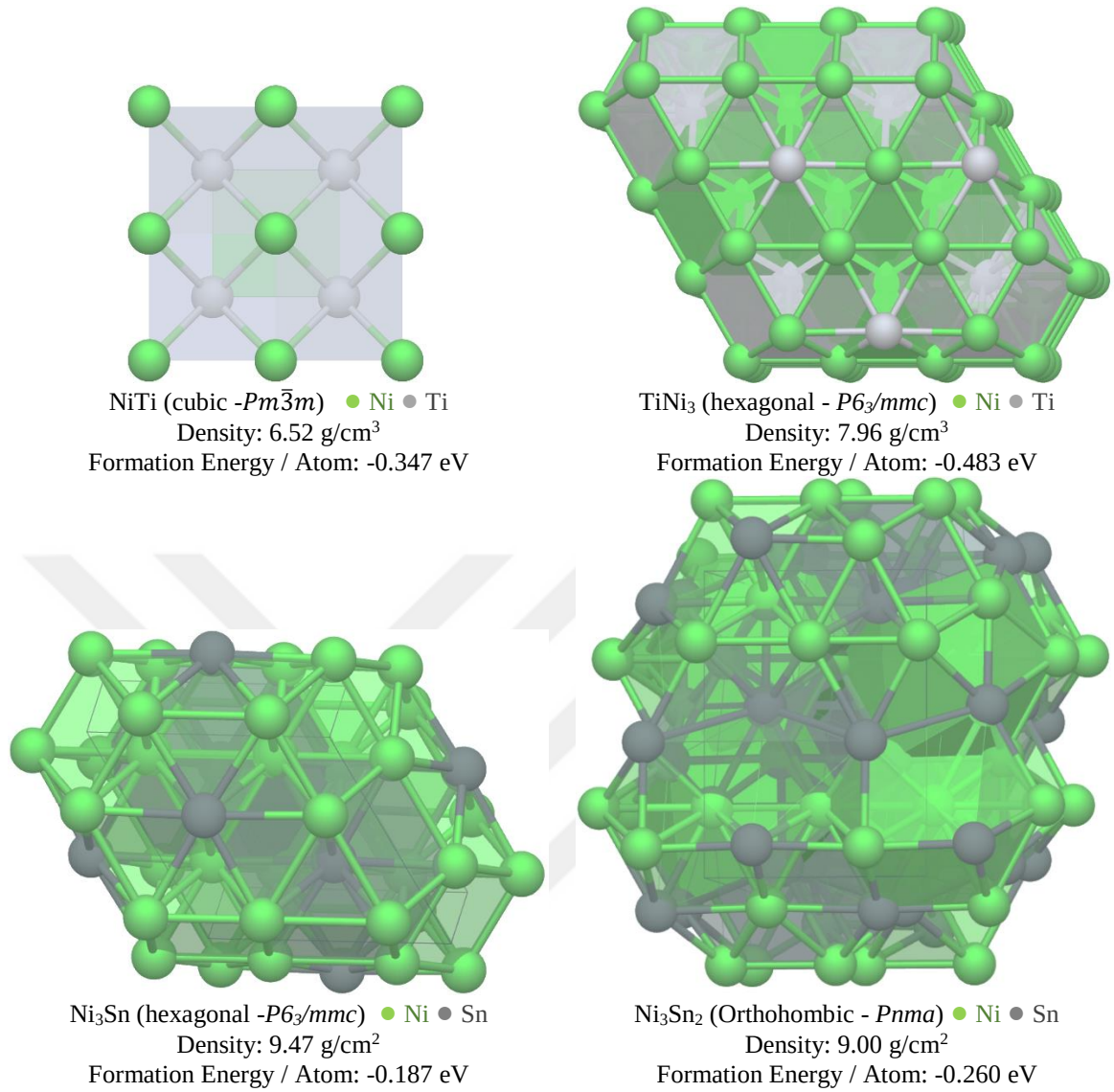


Figure 3.6. The crystal structure, density, and formation energy of all constituents and compounds may exist in NiTiSn alloy [128-138] (continue)

Heusler alloys have been defined in two different crystal structures. Figure 3.7 shows Half-Heusler (HH) TiNiSn and full Heusler (H) TiNi₂Sn crystal structure. Heusler alloys can show various characteristics and their general formulas are XNiSn (for HH) and XNi₂Sn (for H), where X represents one of (Ti, Zr, and Hf element) [139].

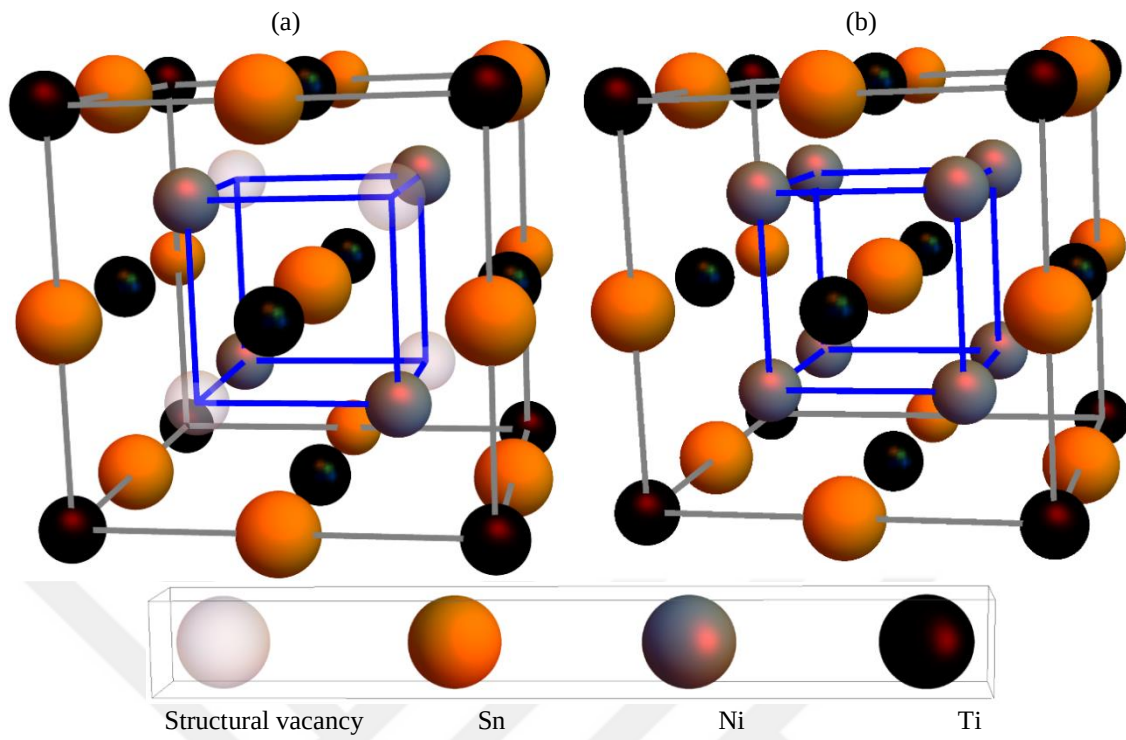


Figure 3.7. (a) Half-Heusler NiTiSn alloy and (b) Heusler TiNi₂Sn alloy crystal structure

4. INSTRUMENTATION

Instrumentation is a general term used for devices that can be used for obtaining physical quantities directly or indirectly through different measuring techniques. All of those devices are based on the fundamental concepts of physics. In the following sections, some related devices that have been used in this study are clarified.

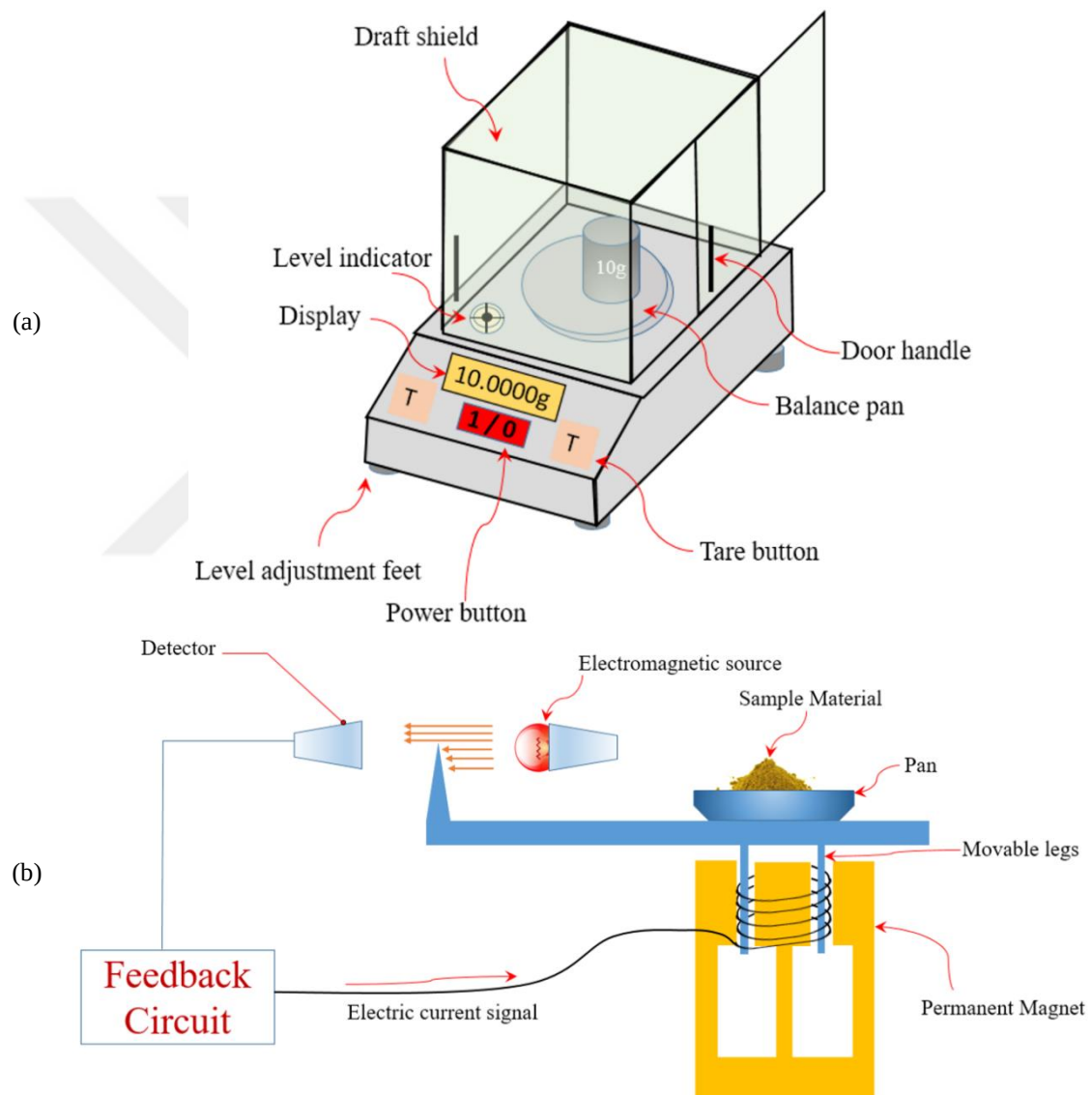


Figure 4.1. Schematic diagram of an analytical balance

4.1. Analytical Balance

An analytical balance is a sensitive balance that can be used for weighing a sufficient amount of materials. Normally electronic balance with 0.0001g precision is used by metallurgists. Figure

4.1a shows a schematic diagram of an electronic balance with a pan that is enclosed with a transparent enclosure (draft shield), which can protect the pan from the current air or unwanted dust in the atmosphere. The balance has a level indicator to be placed on a flat workbench, and sometimes, it can be controlled by using level adjustment feet.

In modern electronic scales, there is only one pan with an electronic circuit, which, while increasing efficiency, makes the size of the device much smaller (Figure 4.1b). There a light detector that detects the incident light coming from a specific light source. The light is normally band with a barrier, and when a specific amount of sample is put on the pan, it forces the pan to downward, thus, a more fractional light can pass from the barrier and the detector can detect more incident light. The incoming light converts to an electrical signal and it is processed in an electric circuit. Then a sufficient electric current is directed to the permanent magnet to return the displaced pan to its null position. Indeed, the measuring weight is not directly obtained, but it is based on Newton's law ($F=mg$), where g is the gravitational acceleration ($\sim 9.8 \text{ m/s}^2$ at sea level).

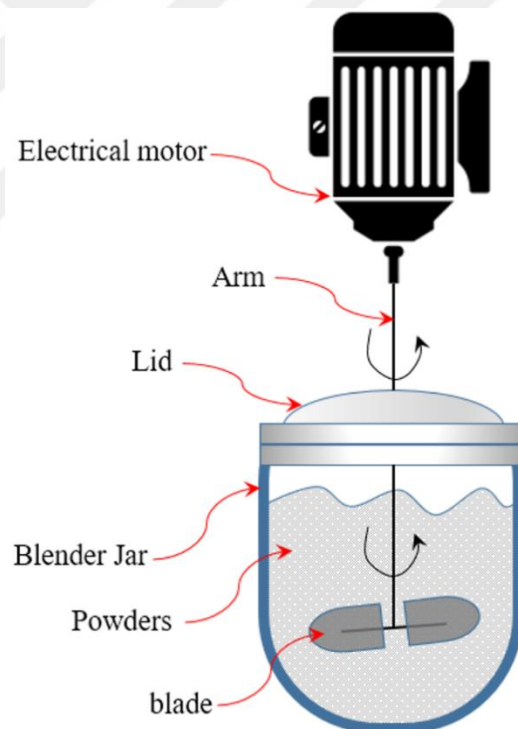


Figure 4.2. Schematic diagram of a mixer with an electrical motor

4.2. Mixture

In powder metallurgy, the mixing process is important to give homogeneity to the obtained alloy. There are some other techniques such as annealing that can be performed at certain high

temperatures, but the pre-mixing process is cheaper and requires a short time compared to the other types of diffusion-based processes.

Figure 4.2 illustrates the schematic diagram for a mixer with an electric motor to rotate the blades. In this stage, only the tiny particles of powders approximately spread uniformly, so atoms must propagate through a sufficient melting process to form an alloy.

4.3. Mechanical Compressor

In most powder metallurgy, raw materials are poured inside a cylindrical mold and pelleted with a pressure of several Mega-Pascal. Figure 4.3 reveals the schematic diagram of a particular manual mechanical compressor. The powders should be carefully poured into the mold. Also, the amount of powder and compression should be sufficient. In low compression, the pellets can have cavities and in an exaggerated force, they may break down. The size of the pellets should be in accordance with the groove of the melting machine.

After the pelletizing process, the specimens can be easily handled for the next manufactured steps. One of the reasons for pelletizing powder is to avoid blowing powders during the melting process, also, it can reduce contamination in high temperatures. Besides, some metals can evaporate during the melting process, therefore it influences the predetermined compositions.

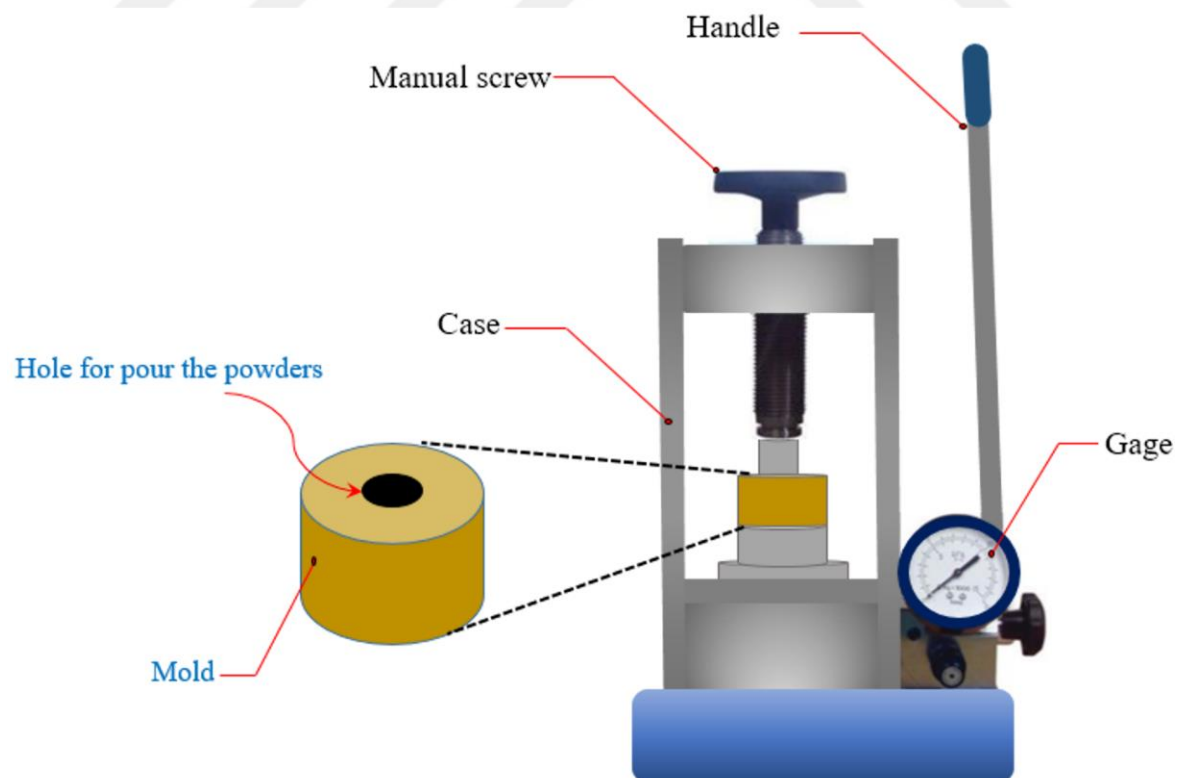
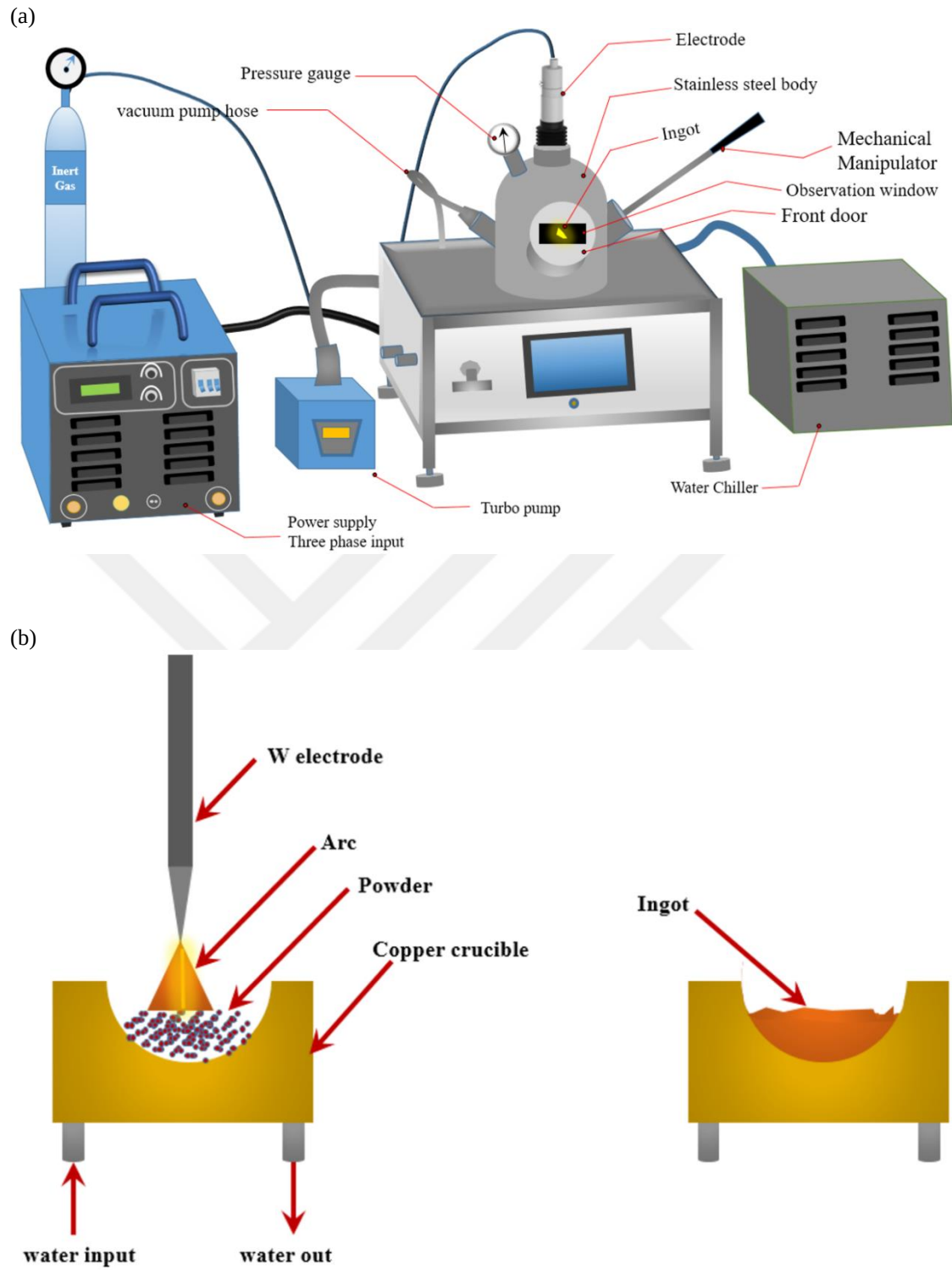


Figure 4.3. Schematic diagram of a manual mechanical compressor



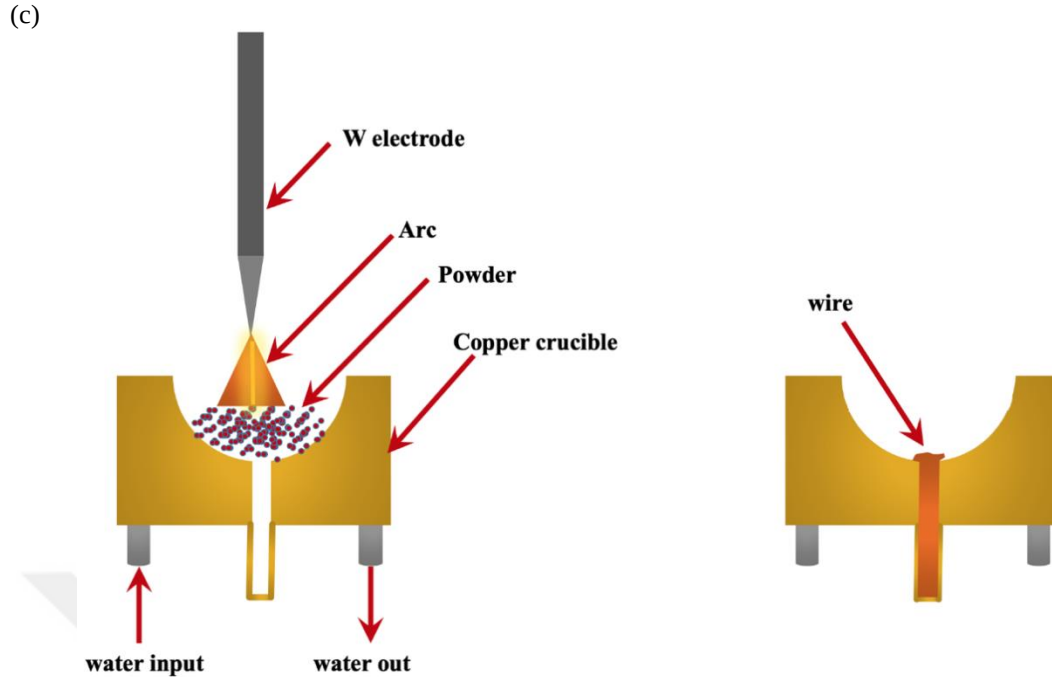


Figure 4.4. (a) A schematic diagram of a vacuum arc remelting system; (b) melting process and producing ingot; (c) wire (continue)

4.4. Vacuum Arc Remelting

Vacuum arc remelting (VAR) is an efficient technique to manufacture alloys for many applications. Since the atmosphere can be controlled through a vacuum chamber and an inert gas can be injected, so contamination can be controlled. The disadvantages of this technique are the time-consuming and high cost. The technique offers production with no porosity and since Ti can easily be oxidized, therefore a controlled atmosphere eliminates these unwanted reactions.

Figure 4.4 illustrates the schematic diagram of a vacuum arc remelting device that consists of a high voltage power supply, a turbopump, and a chiller. In the manufacturing ingot, the following steps are required for a VAR melting process. Firstly, the entire chamber should carefully be cleaned with alcohol and tissue from any unwanted dust or residuals of the latest melting processes. Then, the compacted mixed-powders (pellets) are put in the copper crucible. The stainless-steel chamber is closed and the vacuum pump is turned on. The more the vacuumed chamber, the most ideal ingot product with less pollutes. Then the chamber is filled with argon gas, which necessary as a medium for making a spark between the electrode and the powders (raw material). Argon is better than helium because its atomic weight is bigger, thus it can deliver more energy to the raw materials. Also, argon gas does not react with the raw materials even in the higher temperatures. The chamber pressure normally is chosen less than atmospheric pressure ($<10^5$ Pa), which may because of the evaluated temperature produced in the chamber. After inert gas injection, the electrode is biased using a sufficient voltage and current using a power supply. Since the

electrode is negatively biased and the crucible is positive, so the electron beam travels from the electrode and collides with the argon gas to make an ionized medium, which can be seen as a spark. It can warm the raw material up to a high temperature, which depends on the power supplied. Indeed, the power should be adjusted such that the material is melted. After melting the whole material, it may upside down using the mechanical manipulator. To ensure the homogeneity of the alloy, the melting may repeat several times. A fraction of material may evaporate or disperse inside the chamber that should be ejected using a ventilator, then let the chamber filled by air with the same atmospheric pressure and the ingot is cooled down inside the crucible. Generally, the process takes time, which depends on the efficiency of the vacuum pumps. Producing wire using arc melting is the same. It has a narrow cylindrical mold under the crucible, which is filled with molten powder. It should be noticed that the process of melting should be fast because once the molten powder in the mold has cooled and solidified, the residue cannot flow into the mold (Figure 4.4c).

4.5. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a device that can be used for thermal analysis, differentiate between amorphous and crystalline, polymorph, and eutectic phase transitions of different kinds of materials. Since the specific heat capacity of materials can change in different physical or chemical processes, so it is a key point to detect any changes in the heat flow as a function of time and temperature. DSC can be performed for some purposes, firstly, to ensure that the alloys show shape memory behavior, secondly, to find some phase transformation temperatures directly, and give some other data for calculating some other parameters indirectly.

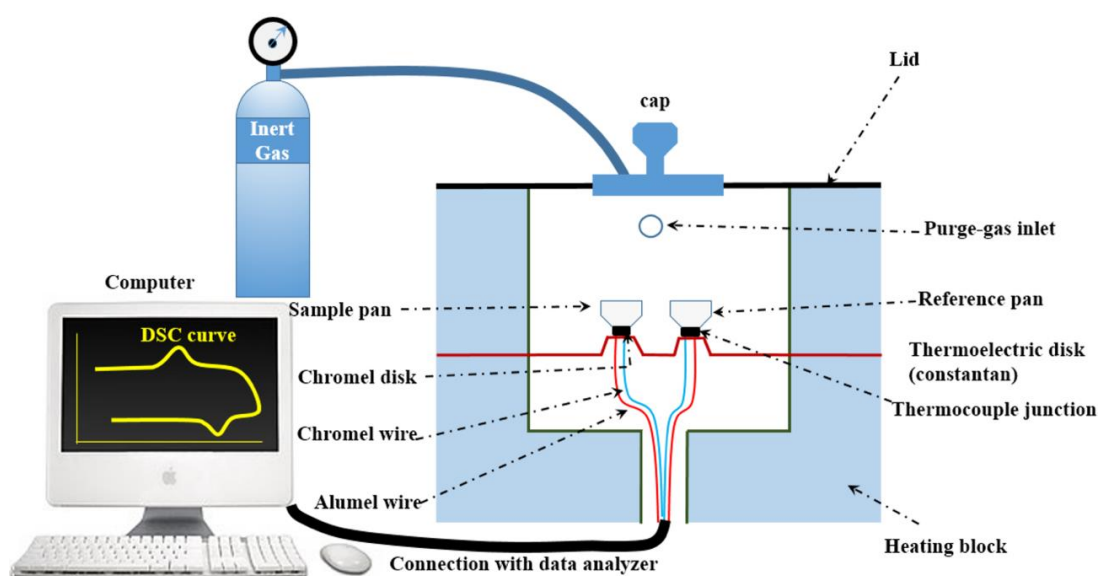


Figure 4.5. Schematic diagram of a DSC device

Figure 4.5 illustrates a general view of a DSC device. It has a chamber that is connected with an inert gas such as Helium or Nitrogen. There is a heater that can be controlled by the given electric power and is fully computerized. The sample normally is put inside a crucible that should be a good conductor of heat and be passive in all environmental conditions. At the same time, a unique empty crucible is used as a reference, which is used to differentiate the temperature change between the sample and the crucible, thus a pure result can be achieved for the sample.

4.6. Thermogravimetric Analysis / Differential Thermal Analysis

Thermogravimetric Analysis / Differential Thermal Analysis (TGA/DTA) is a device that can measure the mass change and other thermal properties of a material in both isothermal and non-isothermal (athermal) processes. The TG/DTA schematic diagram is given in Figure 4.6, where it possesses a heating system based on Joule heating (Ohmic heating), but the cooling process is carried out naturally. The purge gas (e.g. N_2) is used with a constant flowing rate to reduce the oxidation process in the evaluated temperature. However, in a thermogravimetric process to obtain an oxidation layer, pure oxygen or natural air is injected into the chamber.

The TG/DTA device has two sensitive balances, which can determine the mass change in microgram (μg). Normally, the sample is put in a crucible made of passive material, such as aluminum, silver, and platinum, which is based on the type of material. Also, in some DTA cases, the crucible is encapsulated to avoid evaporation, while for the thermogravimetry process the crucibles should be open to allow the mass loss and mass gain by the sample. Some thermal effects of the crucible should be canceled from the sample to achieve a remarkable measurement; thus, the same empty crucible is used as a reference. A sensitive thermocouple is connected to the bottom of the crucibles (sample and reference) to record temperature as a function of time.

Two different measurements can be obtained from this equipment, including thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA can be run for the athermal and isothermal process. In the athermal process, the atmosphere of the sample is not controlled, and the temperature is increased at a constant rate (K/min). The different oxidation (mass gain) or reduction (mass loss) can be detected as a function of temperature. The thermogram results can be analyzed by software and some basic calculation can be carried out. Sometimes, there is a benefit to know the behavior of the sample at a specific temperature. Although some materials in some particular range of temperature have a rare or no reaction, in most cases, the material reaction (e.g. oxidation) becomes saturated after a while. The results can be plotted in a two-dimension diagram such that the y-axis and x-axis represent mass change and temperature (or time), respectively.

On the other hand, DTA needs a controlled atmosphere, therefore pure gas is used throughout the measurement process. This measurement can also be performed using DSC, however, DSC

cannot be used in high temperatures (>400 °C) while the DTA can only be used for the heating process. Besides, DTA shows phase transformation from martensite to austenite phase in an SMA but the martensite phase transformation cannot be achieved unless using a chiller device. The data can be plotted such that the y-axis represents temperature and the x-axis represents time.

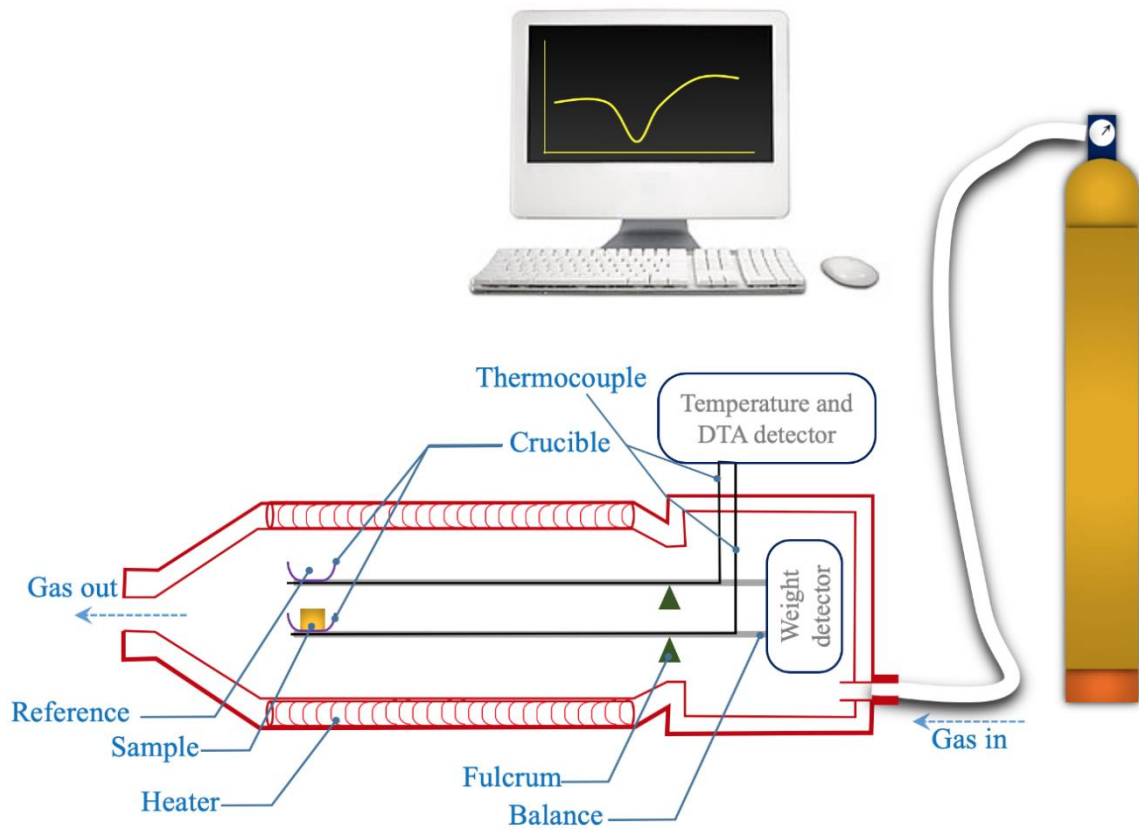


Figure 4.6. A Schematic diagram of a TG/DTA system

4.7. X-ray Diffraction (XRD)

The crystal structure of material impacts the mechanical and other physical properties of a material. For example, the change in crystal structure between the austenite and martensite phases of an SMA is the main reason for the shape memory effect. This crystal structure can be determined by X-ray diffraction (XRD) measurements that based on Bragg's law ($\lambda = 2d \sin \theta$), where λ is the wavelength of the X-ray, d is the interplanar distance of the crystal, and θ is Bragg's angle. Since X-ray has a short wavelength, so it can be used for finding crystallographic purposes. Figure 4.7 presents a general view of an X-ray tube and how the X-ray diffraction test is performed. The result is a pattern, which directly cannot be understood, but it should be analyzed. The lattice parameters for various elements and compounds are different, thus the results should be indexed by an updated database. Mostly, copper is used for the target in an X-ray tube, and by bombarded electrons, X-

rays are obtained with different wavelengths. However, a monochromatic X-ray is used and the other wavelengths are filtered by the beryllium window.

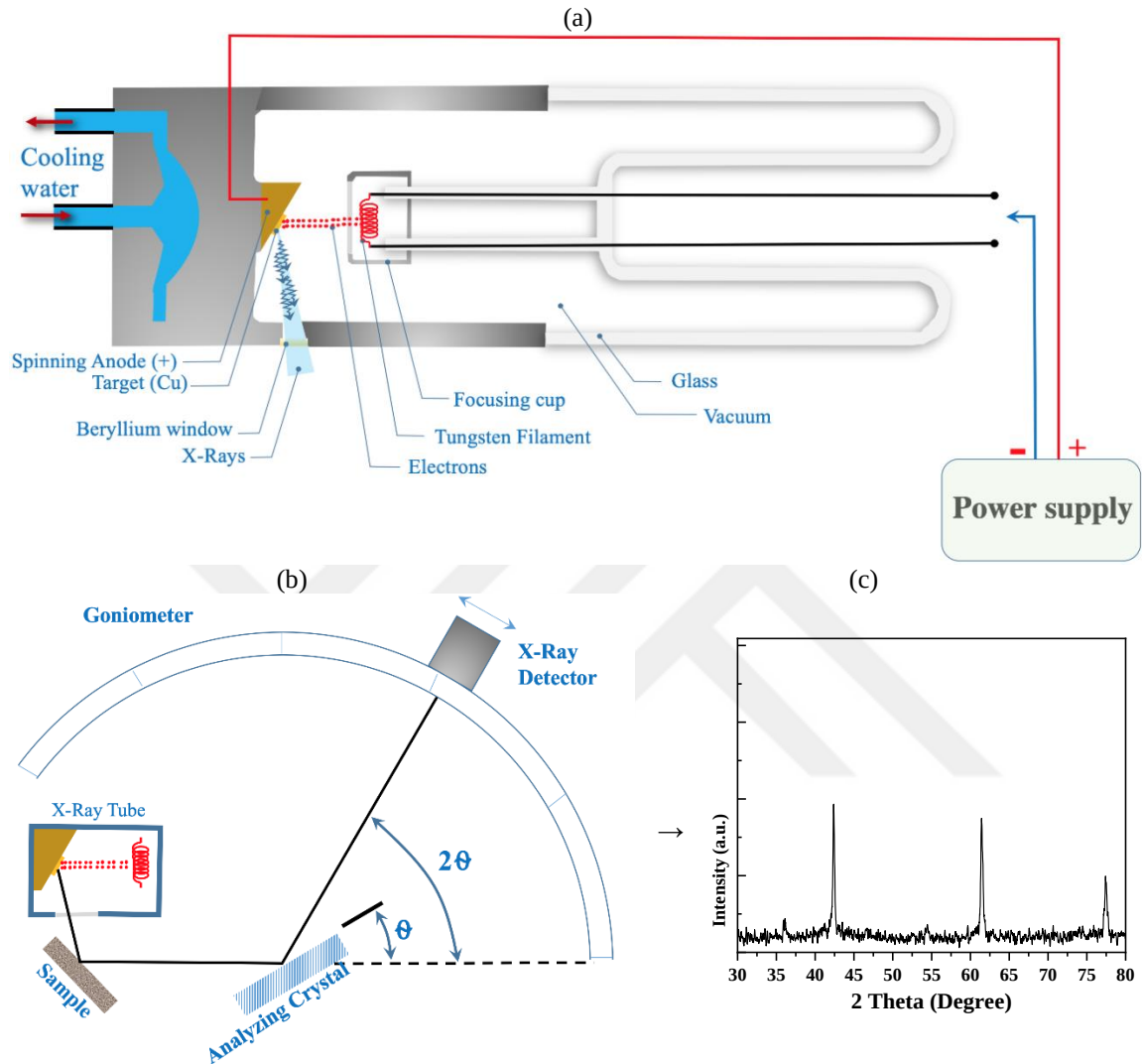


Figure 4.7. (a) A schematic diagram of an X-ray tube, (b) the mechanism of an X-ray diffraction test, and the X-ray pattern of a crystalline sample

4.8. Scanning Electron Microscope – Energy Dispersive X-ray Spectroscopy

The type of crystal structure is an important factor for materials. Besides, microstructures appear during crystallization, which strongly depends on the cooling process. The shape and size of microstructures and their content can be determined by Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDS), respectively. SEM-EDS has a crucial role to achieve a general scan of the surface and obtaining most visual information about a particular material.

Figure 4.8 reveals the schematic diagram of an SEM-EDS device with a particular SEM image. A tungsten-filament generates electrons, then the electrons are accelerated in one direction by an anode. After that, the electrons are concentrated on the sample using a magnetic lens. The position of the electron beam is changed by a scanning coil. When the energetic electrons with high kinetic energy collide atoms on the surface of the sample, they are subjected to different scenarios.

A part of the electrons is elastically scattered by the surface of the specimen and detected by a backscatter electron detector. This part of the measurement is analyzed by a computer to simulate a clear image. This test needs additional pre-works for some samples. For example, if a piece of sample is cut, that cross-section should be smoothed and etched carefully to remove the effects of the cutting process. In addition, for organic materials or ceramic materials (e.g. TiO_2) the surface of the specimen should be gold or silver coated to discharge electrons that accumulated on the surface.

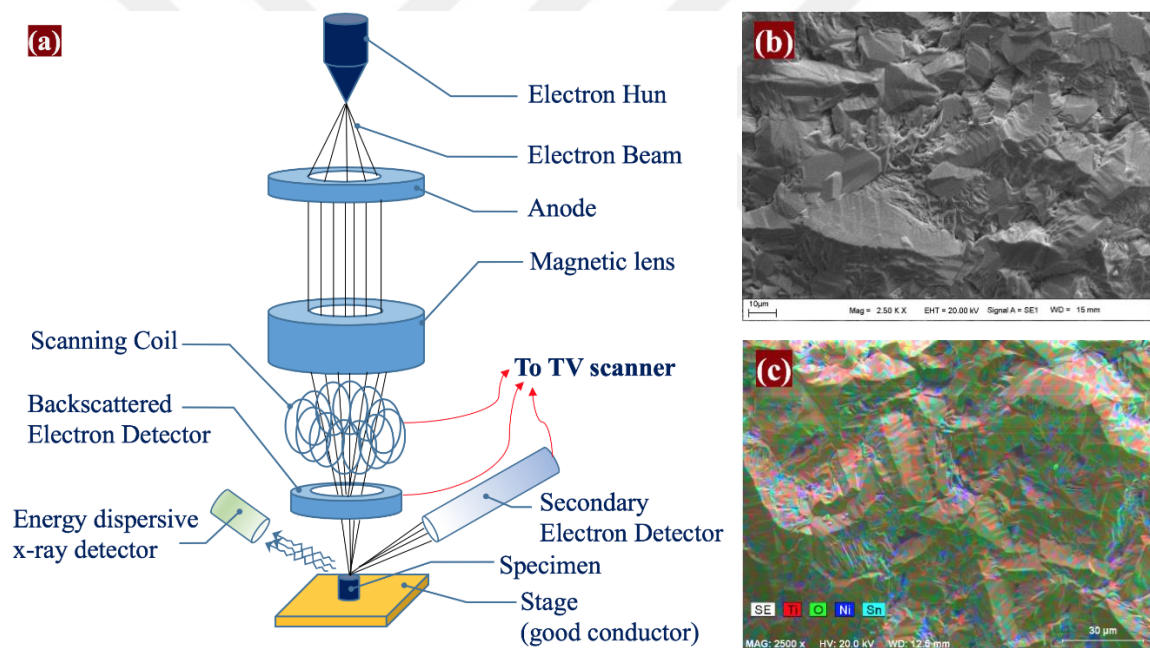


Figure 4.8. (a) A schematic diagram of an SEM-EDS device, (b) a particular SEM image with a magnification of 2500x, and (c) a map of the separation of constituents

Another part of the incident electrons can penetrate the material and they can transfer a part of their energy into the core electrons of atoms. After receiving enough energy, core electrons leave the atom, so their states are filled by other electrons from higher energy levels. Consequently, photons with specific wavelengths are emitted from those particular atoms. These radiations are detected by an energy dispersive X-ray spectroscopy detector. Since each atom has a unique series spectrum, so by analyzing the received patterns, the type of chemical compositions and their concentrations can be accurately specified, especially for heavy metals such as Ni, Ti, Sn, Zn, and

Cu [140]. Besides, a map based on different colors can be obtained to specify how constituents are spread on the surface of the specimen.

4.9. ICP-MS

Inductively coupled plasma-mass spectroscopy (ICP-MS) is a sensitive device that can determine the content of a solution with high precision. ICP-MS can be used for many fields of study, such as medical, material science, and multidisciplinary fields. It can detect a proportion of the elements in part per trillion (ppt) or picogram per milliliter [141]. It can be used for analyzing more than 70 different elements, however, some elements such as hydrogen (H), carbon (C), nitrogen (N), oxygen (O), inert gases, and radioactive elements with an atomic number of more than 92 cannot be analyzed.

There are different geometry and equipped ICP-MS, while a general view of a particular ICP-MS is given in Figure 4.9. An ICP-MS is generally equipped with a solution introduction system, inductively coupled plasma, interface, and mass spectrometer. The measurement is followed by some sequential steps as:

1. In the first step, the liquid sample is atomized by different methods, but mostly nebulizer is used to transfer a small part of the sample to aerosol. The atomization of liquid is as follows: liquid $\rightarrow$ droplets $\rightarrow$ particles $\rightarrow$ molecules $\rightarrow$ atoms. On the other hand, laser, torch vaporization, and electrothermal vaporization are used for solid samples, which are prepared in a standard form (Figure 4.9a).
2. The second part is the ionization in ICM-torch. This method is developed by Fassel and colleagues in the 1970s [142]. In this step, the atoms pass through argon plasma to be ionized. The argon gas is converted to plasma with a temperature around 8000 - 10,000 K using an induction coil (radio frequency load coil or RF load coil – Tesla coil). The Tesla coil is turned around the end of the Torch ICP with three-layer quantize tubes. The plasma is produced in the intermediate tube by heated the argon gas up using an RF coil. The frequency of the RF source is fixed for 4-50 MHz and the given power is arranged around 1-5 kW. The RF coil should be cooled by water. The atomized sample flowed in the inner tube reaches the plasma, and then the atoms are transferred to ions by colliding with the charged argon plasma ($\text{Material} + \text{Ar}^+ \rightarrow \text{Material}^+ + \text{Ar}$), Figure 4.9b.
3. The ionized and unionized material is passed through two or three cons, which are called sampler, skimmer, and hyper skimmer. These cones work as lenses and let a beam of the material pass and preventing the material from decomposing on the other parts of the device, also they increase the sensitivity and stability of the measurement. Due to the presence of these three cones, there is no need to clean the device (Figure 4.9b).

4. In this stage, the filtration of ions is started and only particular ions with m/z can reach the mass spectrometer. Since the entire material that leaving the triple cone is not ionized, so ions are deflected 90° by the Quadrupole Ion Deflector and then interred into the second quadrupole (Collision Reaction Cell, CRC). Neutral materials remain on the same path, so they are eliminated. The second quadrupole is a collision/reaction cell. The third quadrupole is a mass filter and an analyzer. Quadrupole consists of four rods in pairs. Two of them (polar rods) are biased with a DC voltage and an AC voltage is applied to the other pair (hyperbolic rods with radiofrequency). The ion starts fluctuating inside the path. Only specific ions with a determined m/z can pass and the rest removed from the process. This filtration can reach >2400 amu/s [143], Figure 4.9c.
5. The mass spectrometer can detect the arrived ions. It can give the ratio of mass per charge (m/s), which can be analyzed to specify the element. Also, the higher the more number of ions with a particular (m/z) detected by the detector, the higher the peak intensity. Since the detector is photosensitive, so it should be kept in a dark place, Figure 4.9d.

(a)

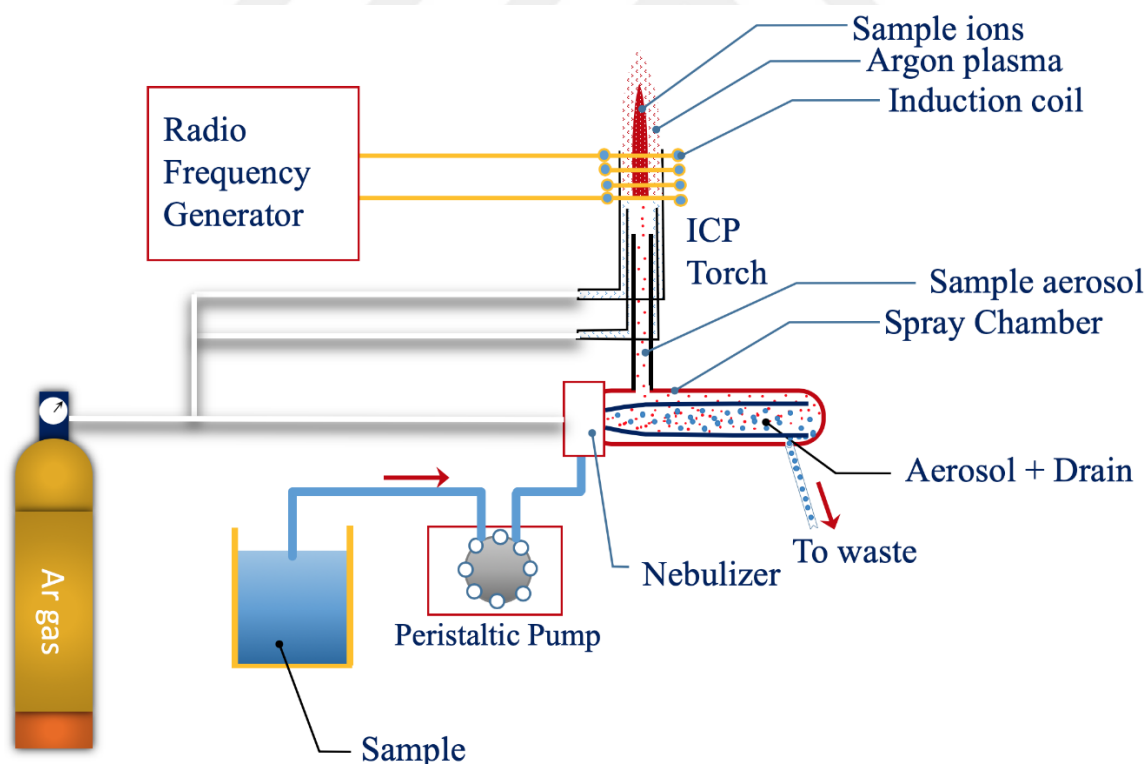
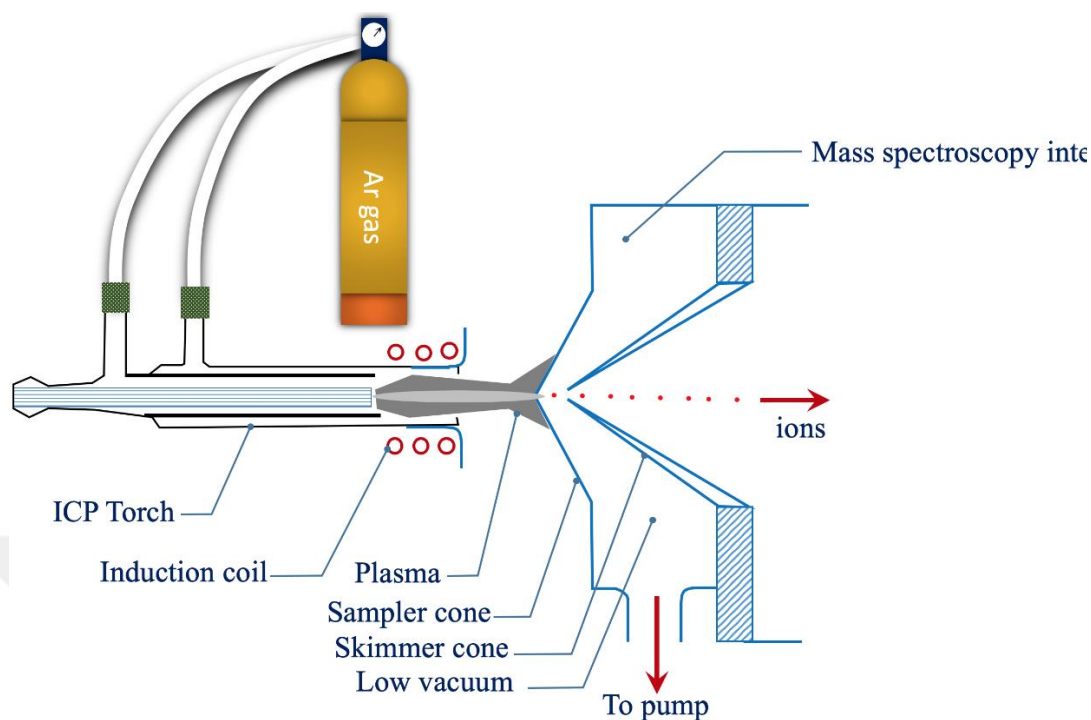


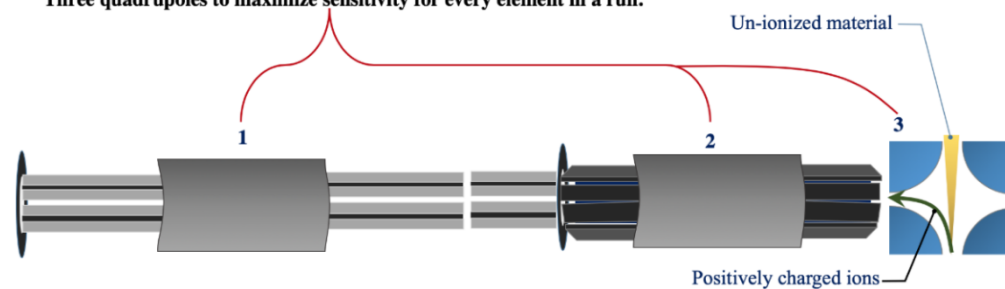
Figure 4.9. A schematic diagram of the key elements of an ICP-MS device. (a) Solution introduction system; (b) inductively coupled plasma; (c) quadrupoles and filtrations; (d) determination of selective elements by a sensitive detector

(b)



(c)

Three quadrupoles to maximize sensitivity for every element in a run.



(d)

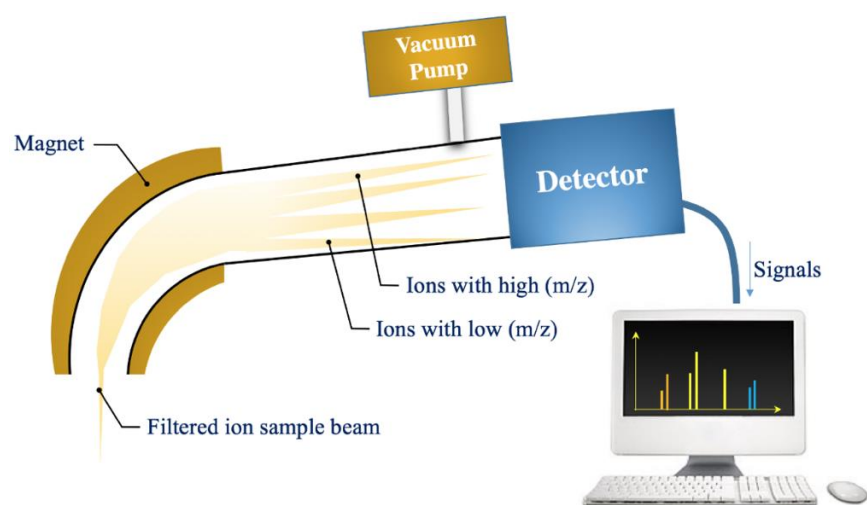


Figure 4.9. A schematic diagram of the key elements of an ICP-MS device. (a) Solution introduction system; (b) inductively coupled plasma; (c) quadrupoles and filtrations; (d) determination of selective elements by a sensitive detector (Continue)

4.10. Potentiodynamic Corrosion Testing

Most corrosion in metals is due to electrochemical corrosion. When a metal is interfaced with an electrolyte, it works as an anodic or/and cathodic electrode. For anodic metal, the atoms oxidized, and thus atoms lose electrons, on the other hand, the electrolyte solution (often O_2 or H^+) was reduced by gain the released electron from the metal. When the number of oxidation and reduction processes reaches the same level, then the net electrical current becomes zero. The oxidation and reduction can occur between two metals with different constituents.

A corrosion reaction needs three essential elements, including an anode electrode, a cathode electrode, and an electrolyte (a conductive solution, which can be alkaline or acidic). Figure 4.10 demonstrates the schematic diagram of a potentiodynamic corrosion test. The test normally is carried out with three electrodes include a working electrode (the sample), reference electrode, and counter electrode. The surface of the metal should be cleaned from dust or unwanted pollutions using acetone followed by ethanol. Then the experiment is set up as shown in Figure 4.10. All electrodes are connected to the potentiostat and it should be kept in mind that the color match each electrode. The counter is used for passing electrical current and its polarity is changed to positive (cathode, where the reduction takes place) or negative (anode, where the oxidation takes place) throughout the experiment. The sample also roles the opposite to counter, therefore the oxidation and reduction can be investigated. The reference is a passive electrical conductor such as Ag/AgCl. The electrical current flowed between the sample and counter electrode is measured, moreover, an electrical potential difference is raised between the sample and the reference electrode, which is measured dynamically using a potentiostat. Some notes should be concerned in the experiment:

- A steady-state open circuit potential is performed to obtain baseline potential. A corresponding software is used for monitoring the potential and current reading of the corrosion environment.
- A beaker provides space for experimentation. The solution is poured inside the beaker and the electrodes are immersed in the solution.
- Bathwater equipped with a thermostat can be used for controlling the temperature
- The area where the sample is in contact with the solution should be obtained. For regular shapes, first, the dimensions are measured and some geometric mathematical rules can be handled to obtain the area while irregular shapes are complicated.

The electric current generated between the anodic and cathodic electrode and the potential differences arises between the sample and reference electrodes. Tafel plot is a relationship between the electric current and potential difference. In such a graph, the y-axis represents the potential difference, and the x-axis represents a direct electric current. Usually, the type of x-axis is selected

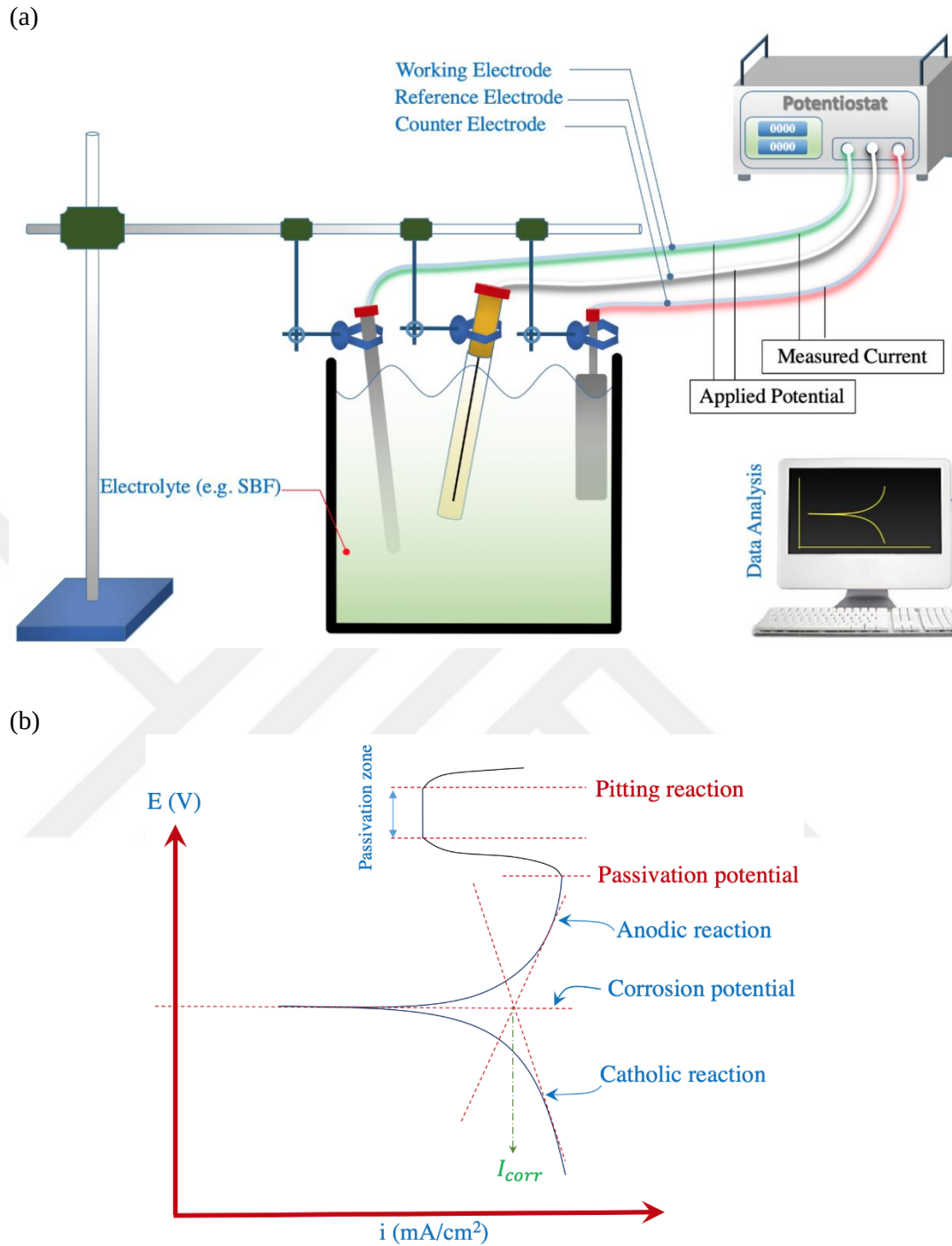


Figure 4.10. (a) The schematic diagram for an electrochemical performing the electrochemical analysis of coating. (b) A particular example of the Tafel test

as a logarithmic scale (Figure 4.10b), since a wide range of current should be recorded throughout the experiment. The theoretical straight lines represent cathodic and anodic reactions, while the curved lines represent the sum of cathodic and anodic electrical current, i.e., the current is obtained with sweep the potential using a potentiostat. In a particular potential, the current looks like a sharp point, where the anodic and cathodic electrodes are flip-flopped. Normally the test begins by

considering the sample electrode as a cathode, then it switched to the anode. In the anode, the increase in the current stop at a particular point, which is called passive potential (E_{pp}). The metals can interact with oxygen to form an oxide layer, which works as a barrier to the further reduction process. During oxide layer production, the current decreased again and then stops. Then a sharp increase in potential can be detected which is called the passivation zone. In some cases, some small areas on the oxide layer break down and the corrosion process starts again, which is called pitting corrosion and the potential is called pitting potential (E_{pit}) [144, 145].

The open-circuit potential is a measurement run to find the equilibrium potential of the specimen in the electrolyte. The test is carried out before the corrosion test. An external voltage is not applied throughout the OCP measurement that is why it has gotten this name. Immersion time is a time in which a sample is put inside an electrolyte in an OCP measurement. The time depends on the nature of the specimen, temperature, and the type of electrolyte solution. Some important dynamic parameters can be found indirectly in the Tafel experiment.

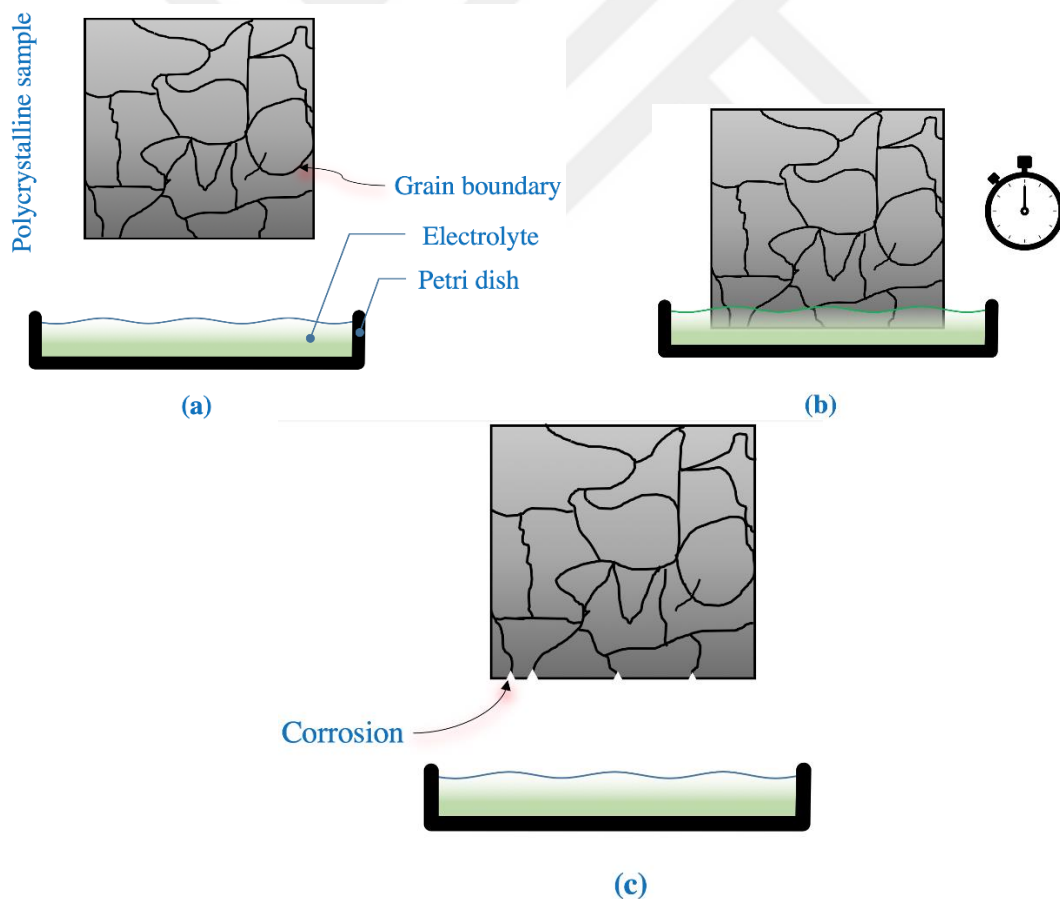


Figure 4.11. A schematic diagram of the etching process. (a) A polycrystalline sample and an acidic medium; (b) etching process; (c) a sample with specifying grain boundaries

4.11. Etching

In the etching process, the grain, grain boundary, and solution play the role of cathode, anode, and electrolyte, respectively. This process works as an active-passive concentration cell in which the atoms in the grain boundaries oxidized and the atoms in the grains reduce. Corrosion is taken place for the active anodes (grain boundaries), and thus, the groove is developed in the grain boundaries. Figure 4.11 reveals the etching process for a polycrystalline metal. Based on the sample and the electrolyte, the immersion time is varied. The etching process usually is performed by metallurgists before performing optical microscopy or scanning electron microscopy on the sample.



5. MATERIALS AND EXPERIMENTAL PROCEDURE

In this chapter, the materials, production technique, and characterization of NiTiSn alloys are explained in detail. Real images of the devices are demonstrated with some necessary detail. Figure 5.1 reveals the schematic diagram of the method from preparation to characterizations.

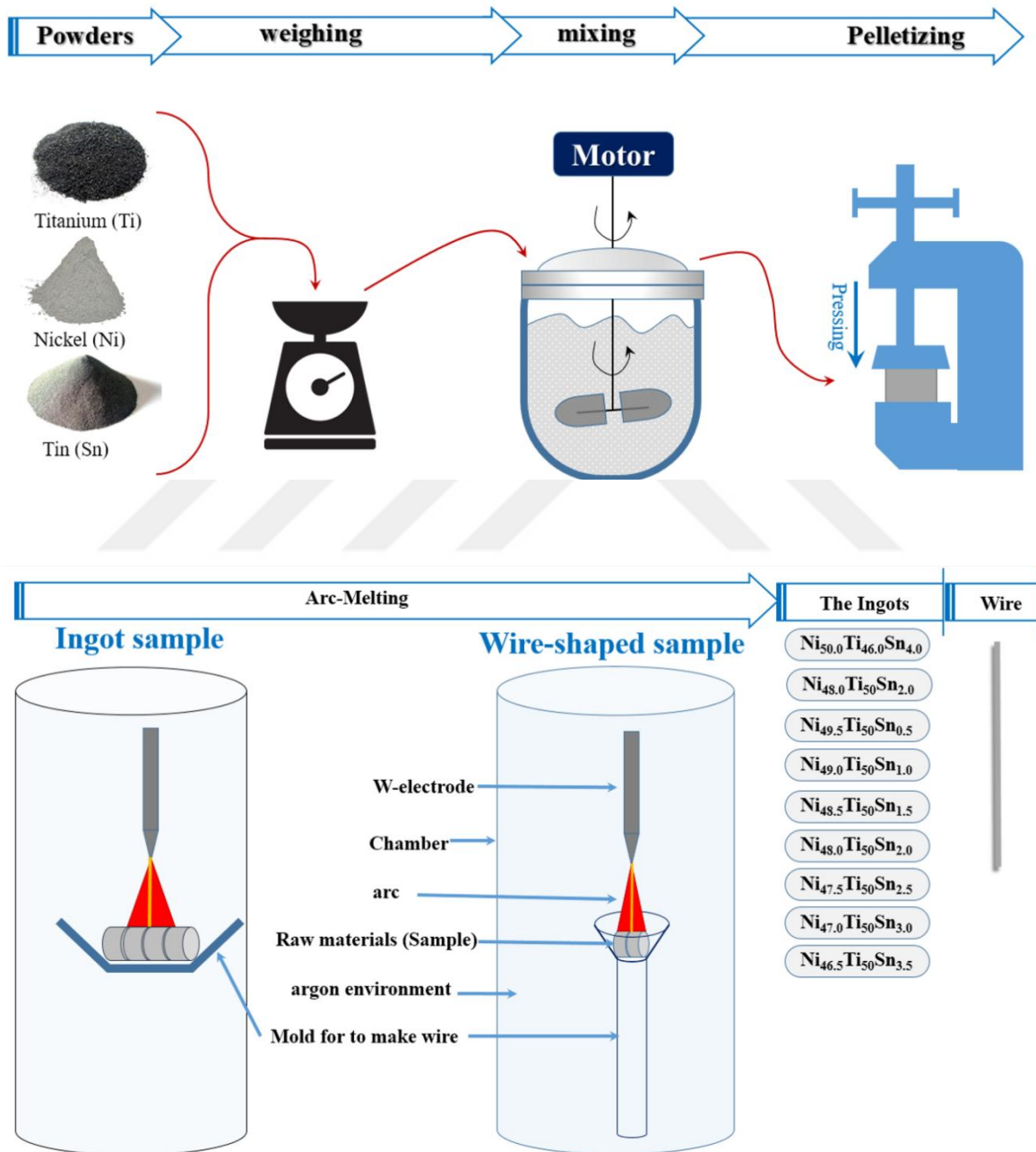


Figure 5.1. Schematic diagram of the production of bulk (ingot) and wire formed NiTiSn alloys

Table 5.1. The alloy's code and compositions (at.%)

Alloys' code	Composition (at.%)		
	Ni	Ti	Sn
Ti-48	50	48	2.0
Ti-46	50	46	4.0
Sn-0.5	49.5	50	0.5
Sn-1.0	49.0	50	1.0
Sn-1.5	48.5	50	1.5
Sn-2.0	48.0	50	2.0
Sn-2.5	47.5	50	2.5
Sn-3.0	47.0	50	3.0
Sn-3.5	46.5	50	3.5
Sn-wire	47.0	50	3.0

5.1. Materials

In this study, three different metallic elements, including nickel (Ni), titanium (Ti), and tin (Sn) were chosen with the purity of 99.99%, 99.5%, and 99.99%, respectively. The powders were purchased from (Sigma-Aldrich). The chosen composition for the alloys is listed in Table 5.1. The corresponding calculation for converting atomic percentage to weight percentage and vice versa has been achieved using the following equations [146]:

$$(at. \%)_x = \frac{(wt. \%)_x / (at. wt.)_x}{\sum_i (wt. \%)_i / (at. wt.)_i} \times 100 \quad (5.1a)$$

$$(wt. \%)_x = \frac{(at. \%)_x \times (at. wt.)_x}{\sum_i (wt. \%)_i \times (at. wt.)_i} \times 100 \quad (5.1b)$$

where (at.%) is an atomic percentage, (wt.%) is weight percentage, x represents the constituent of the alloy, e.g., Ni, Ti, Sn, ...etc., and i represent constituent's series such as Ni, Ti, Sn, ...etc. For example, Eq. (5.1a) and Eq. (5.1b) for the ternary NiTiSn alloy can be written as:

For Ni:

$$(at. \%)_{Ni} = \frac{\frac{(wt. \%)_{Ni}}{(58.693)_{Ni}}}{\frac{(wt. \%)_{Ni}}{(58.693)_{Ni}} + \frac{(wt. \%)_{Ti}}{(47.867)_{Ti}} + \frac{(wt. \%)_{Sn}}{(118.71)_{Sn}}} \times 100 \quad (5.2a)$$

$$(wt.\%)_{Ni} = \frac{(at.\%)_{Ni} \times (58.693)_{Ni}}{(at.\%)_x \times (58.693)_{Ni} + (at.\%)_{Ti} \times (47.867)_{Ti} + (at.\%)_{Sn} \times (118.71)_{Sn}} \times 100 \quad (5.2b)$$

For Ti:

$$(at.\%)_{Ti} = \frac{\frac{(wt.\%)_{Ti}}{(47.867)_{Ti}}}{\frac{(wt.\%)_{Ni}}{(58.693)_{Ni}} + \frac{(wt.\%)_{Ti}}{(47.867)_{Ti}} + \frac{(wt.\%)_{Sn}}{(118.71)_{Sn}}} \times 100 \quad (5.3a)$$

$$(wt.\%)_{Ti} = \frac{(at.\%)_{Ti} \times (47.867)_{Ti}}{(at.\%)_x \times (58.693)_{Ni} + (at.\%)_{Ti} \times (47.867)_{Ti} + (at.\%)_{Sn} \times (118.71)_{Sn}} \times 100 \quad (5.3b)$$

and for Sn:

$$(at.\%)_{Sn} = \frac{\frac{(wt.\%)_{Sn}}{(118.71)_{Sn}}}{\frac{(wt.\%)_{Ni}}{(58.693)_{Ni}} + \frac{(wt.\%)_{Ti}}{(47.867)_{Ti}} + \frac{(wt.\%)_{Sn}}{(118.71)_{Sn}}} \times 100 \quad (5.4a)$$

$$(wt.\%)_{Sn} = \frac{(at.\%)_{Sn} \times (118.71)_{Sn}}{(at.\%)_x \times (58.693)_{Ni} + (at.\%)_{Ti} \times (47.867)_{Ti} + (at.\%)_{Sn} \times (118.71)_{Sn}} \times 100. \quad (5.4b)$$

5.2. Production Process

Some steps were performed to manufacture ingots (balk) and wire-shape NiTiSn alloys. The tools and devices were chosen among comparably highly sensitive available types of equipment. In the following subsections, precise information about the production process has been given.

5.2.1. Weighing the powders

The determined powders were weighed using (SCALTEC Analytical balance SBC 31. 220 g. Readability 0.1 mg. Diameter weighing plate 75 mm). Figure 5.2 shows the balance that possesses a chamber to protect its pan from dust and any current air in the environment. The weight percentage of each constituent is given by:

$$wt.\% X = at.wt. X \times rate\% \quad (5.5)$$

where X is (Ni, Ti, and Sn), and $at. wt.$ is the atomic weight. Also, the total weight percentage of all constituents can be found by:

$$(wt.\%)_{total} = \sum (at.wt. \times rate\%)_x \quad (5.6)$$

The weight of each constituent of the alloys can be calculated using the following equation:

$$wt. (X) = \frac{(wt.\%)_X}{(wt.\%)_{total}} \times alloy\ quantity\ (g) \quad (5.7)$$

The participation of each constituent in the alloy can be easily obtained using Eq. (5.7). In this study, we chose 10 g of powder for each NiTiSn-wire and 5g of powder for the ingot alloys. The results of the calculation are listed in Table 5.2. Since the accuracy of the balance can reach 0.001g, so even one milligram was taken into account.



Figure 5.2. A sensitive digital balance that used to weigh the powders with an accuracy of 1mg

Table 5.2. The calculated weight to prepare a 5 g ingot (bulk) and 10 g wire of NiTiSn SMAs

Alloys' code	Weight (g)			Total Weight (g)
	Ni	Ti	Sn	Ni-Ti-Sn
Ti-48	2.683	2.100	0.217	5.000
Ti-46	2.615	1.962	0.423	5.000
Sn-0.5	2.711	2.233	0.055	5.000
Sn-1.0	2.669	2.221	0.110	5.000
Sn-1.5	2.640	2.197	0.163	5.000
Sn-2.0	2.586	2.197	0.218	5.000
Sn-2.5	2.545	2.184	0.271	5.000
Sn-3.0	2.504	2.173	0.323	5.000
Sn-3.5	2.464	2.161	0.375	5.000
Sn-wire	5.008	4.345	0.647	10.000

5.2.2. Mixing

After preparing all determined powders, the mixing process was performed using a mechanical mixture. In this stage, the powders were well homogenized. Therefore, the final product gained unique specifications. Indeed, this technique contributes to any kind of melting process. Even though, other techniques can be applied after preparing the samples such as hominization in a high-temperature furnace for a convenient period of time. In this study, only mechanical mixing was accomplished.

5.2.3. Pelletizing

In powder metallurgy, pelletizing is commonly used before the melting process. We pelletized the mixed powders using a manual Compressor (Specac Inc., Smyrna, USA). Figure 5.3 shows the compressor with a gauge to monitor the given pressure on the condensed pellets. Approximately 5MPa was applied to make compacted packages of the mixed powders.



Figure 5.3. A manual compressor is used to pelletize the powders into a single pellet

5.2.4. Melting

Arc-Melting Chamber (Edmund Bühler) was used with the following technical characteristics (Figure 5.4): maximum power: 18.5 kW; maximum current: 400 A; volume: 18 liters; vacuum: 10^{-6} mbar; purging gases: He, Ar, or N_2 ; maximum pressure: 1.2 bar. Our samples were produced in an argon atmosphere.



Figure 5.4 The Arc-melting furnace with a high vacuuming chamber and atmosphere control system

Table 5.3. The order, amount, and formula weight of reagents to prepare 1000 mL of SBF

Order	Reagent	Amount	Formula Weight
1	NaCl	8.035 g	58.44
2	NaHCO ₃	0.355 g	84.01
3	KCl	0.225 g	74.55
4	K ₂ HPO ₄	0.176 g	174.18
5	MgCl ₂ .6H ₂ O	0.311 g	203.30
6	HCl	39 mL	—
7	CaCl ₂ .2H ₂ O	0.382 g	147.01
8	Na ₂ SO ₄	0.072 g	142.04
9	Tris	6.118	121.14
10	1.0 M HCl	0-5 mL	—

5.3. Preparation of SBF Solution

To prepare simulated body fluid (SBF), firstly a 700 ml of distilled water (pure water with no mineral additives) was poured in a 1000 ml beaker. Then the water was stirred with a magnetic stirrer and heated up to 309.5 ± 1.5 K (36.5 ± 1.5 °C). The order, amount, and formula weight of reagents for preparing 1000 mL of SBF are given in Table 5.3. The reactants, from 1 to 8, were subsequently added to the distilled water at the determined temperature (36.5 ± 1.5 °C). Each reactant was added into the distilled water after each complete dissolution of the previous reactance, subsequently. The pH of the solution was tested as 2.0 ± 1.0 before adding the 9th Tris reactant. It is proved that a large amount of Tris ((HOCH₂)₃CNH₂) can increase radicals in the solution, therefore calcium phosphate is precipitated. Consequently, the Tris was added to the prepared

solution, when the temperature and pH stayed constant at 309.5 ± 0.5 K and 7.30 ± 0.05 , respectively. The pH was fixed at 7.30 ± 0.05 by adding hydrochloric acid (HCl) dropped to the solution. After adding all the determined Tris, the temperature and pH of the prepared solution were found as 309.5 ± 0.5 K and 7.40, respectively.

Physiological solution (PS), which was found artificially, was also used for the in vitro study. The physiological solution was prepared from (Türk İlaç ve Serum Sanayi A.Ş.). The PS consisted of 0.9 % isotonic sodium chloride solution (154 mmol/L NaCl). Figure 5.5 shows the PS used in this study.



Figure 5.5. Physiological solution

5.4. Corrosion testing

Electrochemical Tefal test was accomplished for Oxide-853K, Oxide-1223K, and Oxide-1498K in both SBF and PS at 310K (body temperature, 37 °C) and room temperature using a Gamry, Interface 1010 B potentiostat (Figure 5.6). The surface of a sufficient piece of as-cast NiTiSn-wire SMA was cleaned from any dust and other unwanted oxide layers using abrasive grain (Silicon Carbide, 2000 G). The sample was washed several times with hexane, acetone, and ethanol, then it dried at room temperature. The electrochemical measurements were performed in a conventional three-electrode cell with SBF and PS (electrolyte solution). The samples were suspended as working electrodes and a Pt rod as the counter electrode. For the first step of the experiment, the as-cast NiTiSn wire SMA was inserted separately into the SBF and PS to achieve a stable open circuit potential (OCP). The silver-silver chloride reference electrode (Ag/AgCl) was utilized as the reference electrode and the Tefal plot was found by scanning from 250 mV, more negative potential, than the OCP at a rate of 0.167 mV/s. The scanning keeps continued in a positive direction up to 250 mV of OCP. In this measurement, some important parameters were obtained

using the Gamry Echem Analyst software, including anodic slope (β_a), cathodic slope (β_c), corrosion current density (i_{corr}), corrosion potential (E_{corr}), and corrosion rate (CR).



Figure 5.6. The Gamry, Interface 1010 B potentiostat



Figure 5.7. (a) A general view of a Lab pipette (Eppendorf Reference "Autoclavable" VARIABLE PIPETTE 100 - 1000 μ l). (b) The front view of the pipette. (c) The pipette tips. (d) Bottles for an in-vitro test

- **In vitro study of the Alloys**

The as-cast NiTiSn-wire, Oxide-853K, Oxide-1223K, and Oxide-1498K SMAs were placed in separate bottles containing (20 ml) of SBF or PS. The amount of solutions were carefully poured inside the bottles using a lab pipette (Eppendorf Reference "Autoclavable" VARIABLE PIPETTE 100 - 1000 μ l), Figure 5.7. Then the bottles were put in an incubator (Figure 5.8), model Electro-

Mag M6040P, for 15 and 30 days at body temperature (311K). 10 ml of the solutions after 15 and 30 days were taken from the bottles for elemental analysis.



Figure 5.8. Incubator for in the vitro study

5.5. Characterization Processes

The characteristic process for the produced alloys is an important step to check the different behavior of the alloys. This process ensures that the alloy delivers essential information about various physical properties of the alloys. The results were compared with the literature to improve the advantages and disadvantages in future studies. For high-quality research, the sensitivity of the devices also should be taken into account. In this study, all devices were chosen from the top sensitive types of equipment and their results have been satisfied. Figure 5.9 illustrates the schematic diagram of the measurements that were carried out in this study.

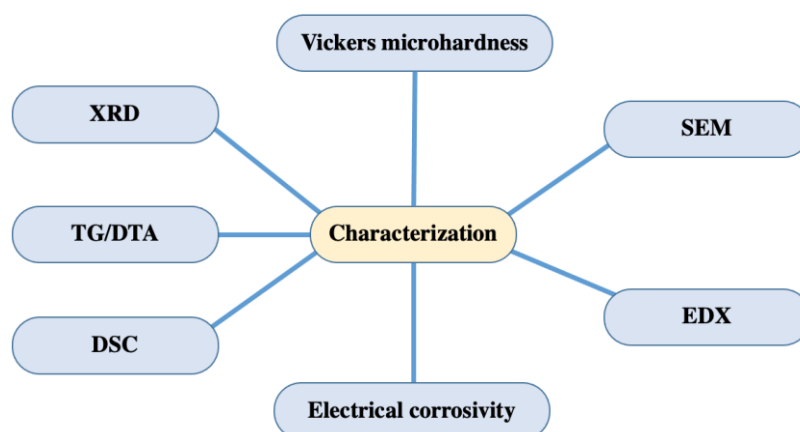


Figure 5.9. Schematic diagram of different measurements for determining characteristics of the alloys

5.5.1. Thermal Analysis

Before performing DSC measurements, the as-cast and oxidized alloys were cut into some fair pieces using an Electric Mini Grinder/Micro Drill (DREMEL) with Emery Cutting Disc (Figure 5.10). NiTi-based alloys generally are harder than some other alloys, such as Cu-based alloys, thus the cutting process took more time and some of the Emery Cutting Discs were broken.



Figure 5.10. Electric Mini Grinder/Micro Drill, DREMEL (*left*), and Emery Cutting Disc (*right*)

The DSC measurements were performed using Perkin Elmer Sapphire Differential Scanning Calorimetry (Figure 5.11a). The measurements for all cases were performed with the aid of purge gas flowed with the rate of 100 mL/min. Normally, nitrogen gas can increase the sensitivity of the measurement because it has a better heat conductivity compared to the other gases, especially for intermediate temperatures. The DSC used in this study could be operated for 223 K (-50 °C) ↔ 673K (400 °C). The chamber equipped with a heater inside and a chiller (PerkinElmer Precisely Intercooler SP Cooling Accessories) was connected in parallel to reduce the temperature to -50 °C (Figure 5.11b). Also, the same aluminum crucibles (P/N SSC000C008, max. temp. to use 600 °C) were used for the reference and sample in the DSC chamber (Figure 5.11c).

Sn0.5, Sn1.0, Sn1.5, Sn2.0, Sn2.5, Sn3.0, and Sn3.5 alloys underwent five complete DSC cycles between 253 K (-20 °C) and 423K (150 °C). The sample weight of Sn0.5, Sn1.0, Sn1.5, Sn2.0, Sn2.5, Sn3.0, and Sn3.5 alloys were 31, 34.4, 74.1, 54.1, 38.6, 62.9, and 38.1 mg, respectively. The heating/cooling rate was 20 K/min for all cases. On the other hand, the as-cast NiTiSn-wire with 80.9 mg was tested with DSC for five complete cycles between 223 K (≈-50 °C) and 373 K (≈100 °C) with a heating/cooling rate of 10 K/min. Also, the oxidized NiTiSn-wire SMAs were tested with the aid of DSC for the temperature range of 223 K (-50 °C) - 423K (150 °C). The heating/cooling rate was also 10 K/min. The weight of samples that oxidized at 853 K (580°C), 1223K (950°C), and 1498K (1225°C) were 57.7, 63.7, 63.7 mg, respectively.



Figure 5.11. (a) the DSC, (b) the chiller (cooling system), and (c) the crucibles used for investigating phase transformations of the alloys

5.5.2. Oxidation

Four small pieces were cut from the as-cast NiTiSn-wire shape memory alloy for the oxidation process. Differential thermal analysis (DTA) measurement was carried out for one of the pieces using Perkin Elmer Pyris Diamond Thermogravimetric/Differential Thermal Analyzer (TG/DTA), Figure 5.12. The measurement was performed for a temperature range of 300K – 1570K. The athermal properties of the sample were performed in the natural atmosphere, so by heating up, three different features were determined, then the starting temperature of those specific athermal behaviors of the sample was chosen for the isothermal process.

The second measurement was thermogravimetry analysis at constant temperatures, including 853 K (580°C), 1223K (950°C), and 1498K (1225°C), which were labeled as Oxide-853K, Oxide-1223K, and Oxide-1498K, respectively. The first step to reaching those particular temperatures was heating the samples with complete atmosphere control. Ni₂ gas was used to cancel all oxidation processes during heating. Then each sample was kept at one of the aforementioned temperatures in the natural atmosphere for 4000s ($\cong$ 67min.).



Figure 5.12. The TG/DTA device used for isothermal oxidation measurements of the NiTiSn-wire sample

5.5.3. Crystal Structural Analysis

The crystal structural analysis for Sn0.5, Sn1.0, Sn1.5, Sn2.0, Sn2.5, Sn3.0, Sn3.5, Oxide-853K, Oxide-1223K, and Oxide-1498K alloys was performed using Rigaku RadB-DMAX II X-ray diffractometer. The measurement was carried out at room temperature for the 2θ range of 30° - 80° and a step size of 2°/min. A monochromatic X-ray (Cu K α) was utilized that has a wavelength of (0.15406 nm). Figure 5.13 illustrates the X-ray diffractometer used in this study, which could be controlled with the aid of a computer. The device has also the following features:

- ✓ X-ray source 1.5 kV power supply,
- ✓ Parabolic Filter,
- ✓ Threshold=3.0,
- ✓ Cutoff=0.1%,
- ✓ BG=3/1.0,
- ✓ Peak-Top=Summit.

Indeed, the XRD patterns can be analyzed by Braggs law, and the pattern has three crucial information, which are: the intensity of the peaks, the angle of the peaks, and the width of the peaks.



Figure 5.13. XRD device used for determining crystal structures of the samples

5.5.4. Microstructural and Compositional Analysis

Sufficient pieces from Sn0.5, Sn1.0, Sn1.5, Sn2.0, Sn2.5, Sn3.0, Sn3.5, and as-cast NiTiSn-wire were sectioned from the as-cast alloys for microstructural and compositional examinations using SEM-EDX. For a clear SEM image, the samples need to undergo coarse grinding, fine grinding, polishing, and etching process. Firstly, the specimens are mounted in a mold (Figure 5.14a). A single sample was positioned face down in the cylindrical mounting and about 2 cm of the mold was filled with epoxy resin and hardener. After about 30 min, the epoxy resin hardened. For grinding and polishing specimens, emery paper (silicon carbide paper) with different grids, including 600, 1000, and 1500, and polishing cloth, were utilized with a metallographic sample grinder polisher machine (Figure 5.14a, Figure 5.14b, and Figure 5.14c). The grinding process was carried out on a wet surface of the emery paper, and diamond paste was utilized during the polishing of the specimens' surface. Then the specimens were etched into HNO₃, HF, and H₂O in a ratio of 4:1:5, respectively. The SEM-EDS test was performed directly on the Oxide-853K, Oxide-1223K, and Oxide-1498K specimens without any further pre-work.

The surface of Sn0.5, Sn1.0, Sn1.5, Sn2.0, Sn2.5, Sn3.0, Sn3.5, as-cast NiTiSn-wire, Oxide-853K, Oxide-1223K, and Oxide-1498K were scanned with SEM-EDS instrument (Model EVO 40XVP coupled with Quantax software and EDS detector) at room temperature (Figure 5.15). Silver paint was used for making electrical conduction between samples and the base (Figure 5.16). The chamber of the SEM-EDS device was vacuumed and then the surface scan was accomplished in different magnifications. Additionally, EDS measurement was performed to obtain the composition of various microstructures. For Sn-0.5, Sn-3.5, and the as-cast NiTiSn alloy, mapping measurement was performed to achieve how different constituents spread in the alloy.



Figure 5.14. (a) Reusable plastic mold and a mounting example; (b) an emery paper; (c) polishing cloth; (d) metallographic sample grinder polisher machine

5.6. Trace Element Analysis

Since the alloys include Ti, Ni, and Sn elements, so for both SBF and PS the trace element analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS) Perkin Elmer model (NexION 350X, USA) with a universal cell technology (UCT) and model solutions. Figure 5.17 shows the ICP-MS device used in this study. The analytical signal of elements was measured in standard/KED and collision modes and the selection of the effective correction conditions of the polyatomic interferences was performed by defining the optimal helium flow rate in the range from 0.5 to 3.5 mL/min. For ICP-MS analysis. 2.5 ml of 65% HNO_3 (nitric acid) was added into 1 mL of the solution and the DAPs were shaken for about 1200 s (20 min.) then the covers were closed. The final volume of the obtained solution was completed to 10 mL with ultrapure water. For the Ni and Sn element, 1 mL of the solutions were taken and again diluted with ultrapure water to a final volume of 10 ml and the reading was done on the device. For the Ti

element, 0.5 ml was taken and diluted again with ultrapure water to a final volume of 10 mL and the reading was done on the device.



Figure 5.15. Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry (SEM-EDX) used for the morphology of microstructures and their chemical compositions

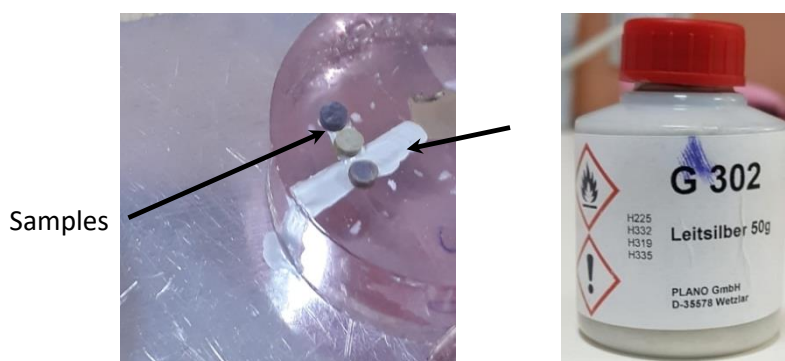


Figure 5.16. The molded samples (*left*) and the electric conductive silver paint used in the SEM measurements (*right*)



Figure 5.17. The ICP-MS is used for measuring the concentration rate of elements in SBF and PS.

Table 5.4. The operating conditions of the ICP-MS

Component / Parameter	Type / Value / Mode
Nebulizer	MEINHARD (concentric)
Spray Chamber	Glass Cyclonic
Triple Cone Interface Material	Nickel
Plasma Gas Flow	18.0 L/min
Auxiliary Gas Flow	1.2 L/min
Nebulizer Gas Flow	0.84 L/min
Sample Uptake Rate	1 mL/min
RF Power	1150 W
Integration Time	600 ms
Replicates per Sample	3
Mode of Operation	STD/KED Mode Collision (using He gas)

For the ICP-MS measurement, the following burning procedure was applied:

- Increased to 160 °C for 5 min.
- It was kept at 160 °C for 5 min.
- Increased to 190 °C for 1 min.
- It was kept at 190 °C for 10 min.
- Cooled to 50 °C.

Table 5.4 gives some information about the characteristics of the ICP-MS used for this study [147]. The instrument had three cones to supreme tightly focus ion beam into the quadrupole and avoid sample deposition on the inner parts. Also, the device could deflect the ion beam 90° into the Universal cell to remove all neutral atoms that may pass through the cones.



6. RESULTS AND ANALYSIS

The study consists of two stages, which have been separately discussed. In the first section of this chapter, the results of different characterizations of the bulk (ingot)-formed NiTiSn shape memory alloys have been explained, and in the second section, the wire-shaped NiTiSn shape memory alloy has been discussed. Besides, some other theoretical calculations have been carried out and the results compared with the literature.

6.1. Bulk-Formed NiTiSn SMA

The ingots of NiTiSn SMAs were produced with seven different compositions in a regular sequence. The alloys arranged from lower Sn content to high Sn content, such that 0.5 at.% Sn, 1.0 at.% Sn, 1.5 at.% Sn, 2.0 at.% Sn, 2.5 at.% Sn, 3.0 at.% Sn, and 3.5 at.% Sn. In the following sub-sections, all characterization results have been discussed.

6.1.1. DSC results

The small pieces were cut from the ingots and then DSC measurement was run for five complete cycles in a particular temperature range and heating/cooling rate of 10 K min⁻¹. The aim of the cycling with the same speed was to find the thermal stability of the alloys, i.e., for less shifting in the thermal behavior of the alloys, such as transformation temperatures and enthalpy change, the shape memory alloys showed more thermal stability.

Figure 6.1 demonstrates the DSC results of the ternary Ni-Ti-Sn shape memory alloys. In all cases, only a single-phase transformation represents martensite to austenite (reverse phase transformation or endothermic process) and austenite to martensite (forward phase transformation or exothermic process). Since B19' represents the martensite phase and B2 represents the austenite phase in NiTiSn alloy, so the phase transformation can be expressed as: for the reverse and forward phase transformation, we obtained (B19'→B2) and (B2→B19'), respectively. B2 and B19' belong to Pm-3m [60] and P21/m [148] space groups, respectively.

Many researches, conducted on binary NiTi shape memory alloys, have reported a two-step phase transformation in the forward, reverse, or both [149, 150]. Binary NiTi alloys illustrate an intermediated phase (R-phase) that has a different crystal structure and disappear by the continuing process. R-phase has $P\bar{3}$ space group [151]. It is reported that dislocations are formed during the DSC cycling process [21, 152, 153]. We did not perform the annealing process for the as-cast NiTiSn ingots at high temperatures, thus it may affect the microstructures of the alloys. On the other hand, Kim et al. [38] achieved a two-step phase transformation in the exothermic process. They alloyed NiTi SMA with 5, 8, 10, 12.5 at.% Sn element and then they annealed the samples at

1273 K. The DSC result showed a two-step phase transformation, which may because of the formation of Ti_3Ni_4 precipitated phase coherently in the matrix of the alloys [154].

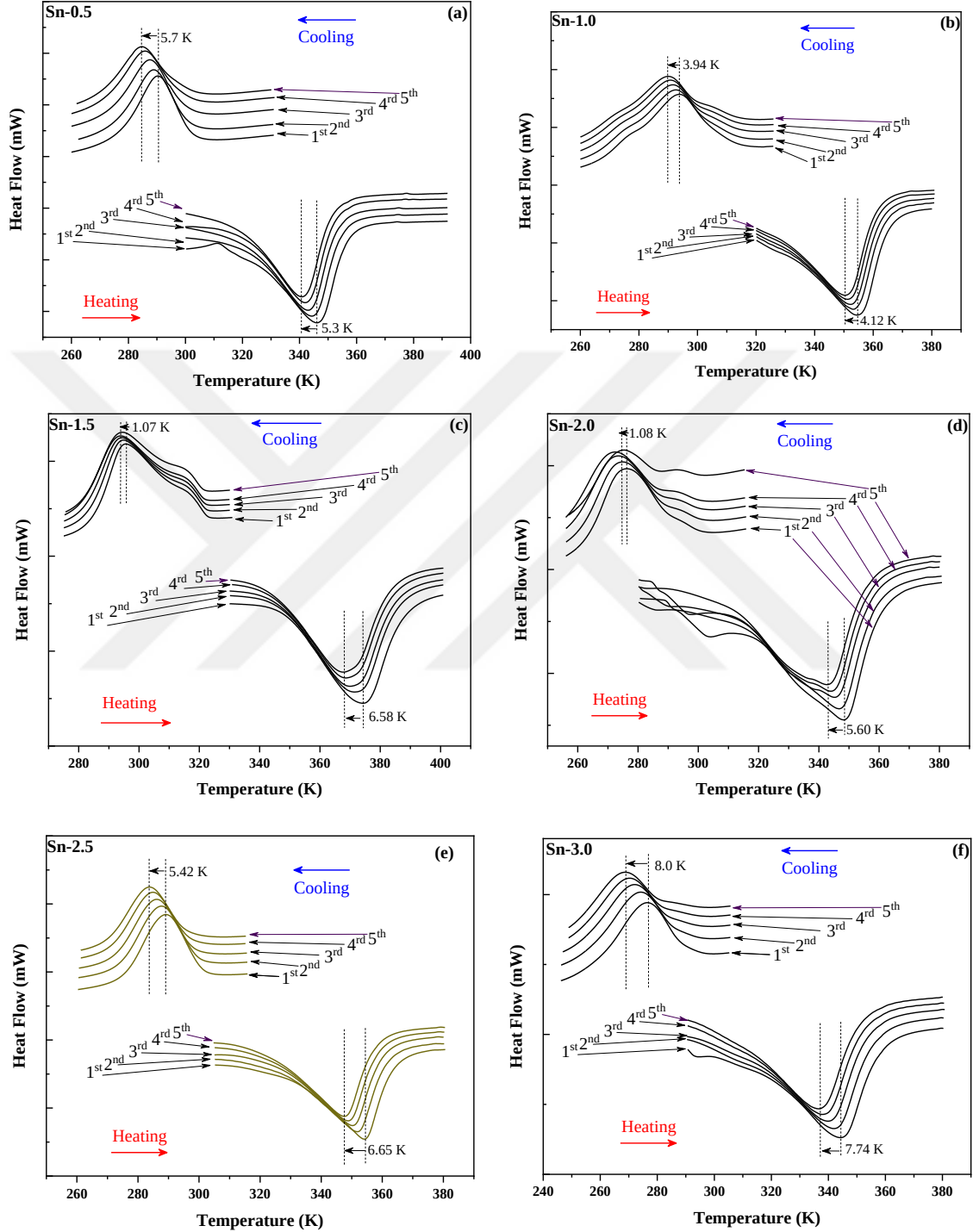


Figure 6.1. The results of five sequence cycling DSC for (a) Sn-0.5, (b) Sn-1.0, (c) Sn-1.5, (d) Sn-2.0, (e) Sn-2.5, (f) Sn-3.0, and (g) Sn-3.5

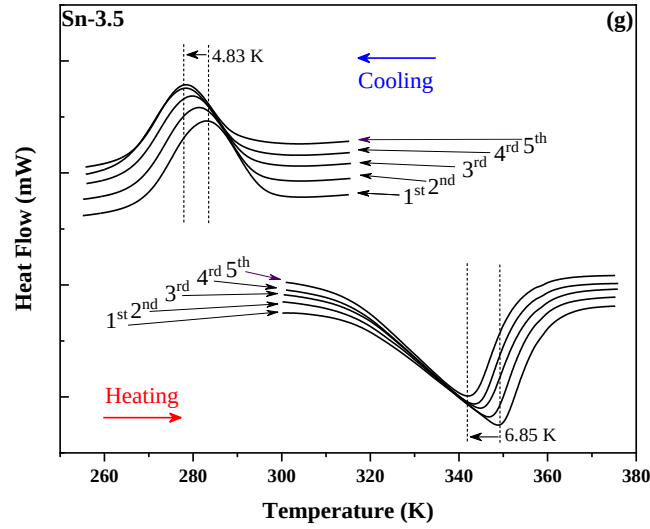


Figure 6.1. The results of five sequence cycling DSC for (a) Sn-0.5, (b) Sn-1.0, (c) Sn-1.5, (d) Sn-2.0, (e) Sn-2.5, (f) Sn-3.0, and (g) Sn-3.5. (Continue)

After five complete DSC cycles, the austenite and martensite peaks were shifted in the range of 4-7.5K and 1.07-8K, respectively. In general, these shifts in transformation temperatures were increased by increasing the Sn additive into the NiTi-based shape memory alloy (Figure 6.2a). The phase transformation profile of the alloys is listed in Table 6.1, which consists of martensite finish (M_f), martensite peak (M_p), martensite start (M_s), austenite start (A_s), austenite peak (A_p), and austenite finish (A_f) temperatures. These phase transformation temperatures are shifted to the lower temperature through the DSC cycle process. Figure 6.2b demonstrates the A_p and M_p for all specimens, where the phase transformation temperatures have experienced a slight reduction by increasing the DSC cycle process. Miyazaki et al. [19] stated that the martensite finish temperature of NiTi SMA continuously diminished and reached a plateau after 10 cycles. They returned these variations in phase transformation temperature to increase the formation of dislocation in the alloy. Tong and colleagues [20] improved the thermal stability of a binary NiTi SMA by alloying with an expediated fraction of copper and niobium. The result remarkably displayed that the stability of the alloy was improved such that the A_p and M_p temperatures only shifted less than 0.3 K.

Enthalpy of a system changed throughout the phase transformation processes. Generally, the total energy of the system increases (gain energy) and decreases (expel energy) during reverse and forward martensitic phase transformation processes, respectively. In the non-isothermal DSC measurement, the change of enthalpies can be detected in the DSC pattern, where the trough (in the heating direction) represents endothermic enthalpy change and peak (in the cooling direction) represents exothermic enthalpy change. In the chosen operational temperature range, the shape memory alloys showed a phase transformation between the austenite and martensite phases, which

Table 6.1. Phase transformation temperatures, enthalpy change, and Gibbs free energy of Sn0.5, Sn1.0, Sn1.5, Sn2.0, Sn2.5, Sn3.0, and Sn3.5 alloys

	Cycle no.	Sn-0.5	Sn-1.0	Sn-1.5	Sn-2.0	Sn-2.5	Sn-3.0	Sn-3.5
M_f	1 st	276	271	286	264	276	263	269
	2 nd	276	271	294	261	274	258	268
	3 rd	273	270	283	259	273	256	267
	4 th	271	269	282	258	271	255	265
	5 th	271	269	282	263	271	255	267
M_p	1 st	290	294	295	276	289	277	283
	2 nd	290	293	295	275	288	274	282
	3 rd	288	292	294	274	286	272	280
	4 th	286	291	294	273	285	270	278
	5 th	285	290	294	275	283	269	279
M_s	1 st	302	309	320	289	301	288	296
	2 nd	302	307	319.8	287	300	285	295
	3 rd	301	306	318.3	287.8	299	283	293
	4 th	299	304	318.8	285	298	281	291
	5 th	298	303	319.2	285	296	279	290
A_s	1 st	322	338	349	319	331	324	319
	2 nd	324	337	347	317	328	321	318
	3 rd	325	336	347	315	327	321	317
	4 th	323	335	346	312	325	318	317
	5 th	322	334	346	311	323	316	315
A_p	1 st	346	355	375	349	354	345	349
	2 nd	346	353	372	347	352	342	347
	3 rd	343	352	370	346	351	340	345
	4 th	342	351	369	344	349	338	344
	5 th	341	350	368	343	348	337	342
A_f	1 st	357	365	386	362	363	358	359
	2 nd	357	363	385	358	362	355	358
	3 rd	354	363	384	360	360	353	356
	4 th	352	362	382	358	359	351	355
	5 th	351	361	381	358	357	351	354
$\Delta H^{A \rightarrow M}$ (J/g)	1 st	21.9	21.7	26.2	19.6	24.2	20.8	21.7
	2 nd	20.2	21.1	26.4	20	23.4	18.1	20.8
	3 rd	20.8	20.9	25.4	18.1	22.8	20.4	20.5
	4 th	20.2	20.2	25.9	19.5	23.2	17.7	21.3
	5 th	17.9	20.6	25.9	14.6	20.4	23.6	20.0
$\Delta H^{M \rightarrow A}$ (J/g)	1 st	17.6	23.5	24.7	14.9	22.8	16.2	19.9
	2 nd	19.1	19.2	25	18.4	22.8	25.8	22.4
	3 rd	21.9	22.7	24.7	14.4	22.4	21.5	22.1
	4 th	17.1	22.2	24.9	17.5	24.0	25.2	21.3
	5 th	22.7	23.1	25.2	19.1	24.3	19.5	22.6
$\Delta G^{A \rightarrow M}$ (J)	1 st	1469	1953	2309	1688	2129	1752	1914
	2 nd	1594	1605	2313	2023	2135	2826	2161
	3 rd	1772	1934	2311	1621	2074	2381	2145
	4 th	1392	1933	2246	1993	2228	2819	2110
	5 th	1854	2018	2224	2148	2270	2702	2246

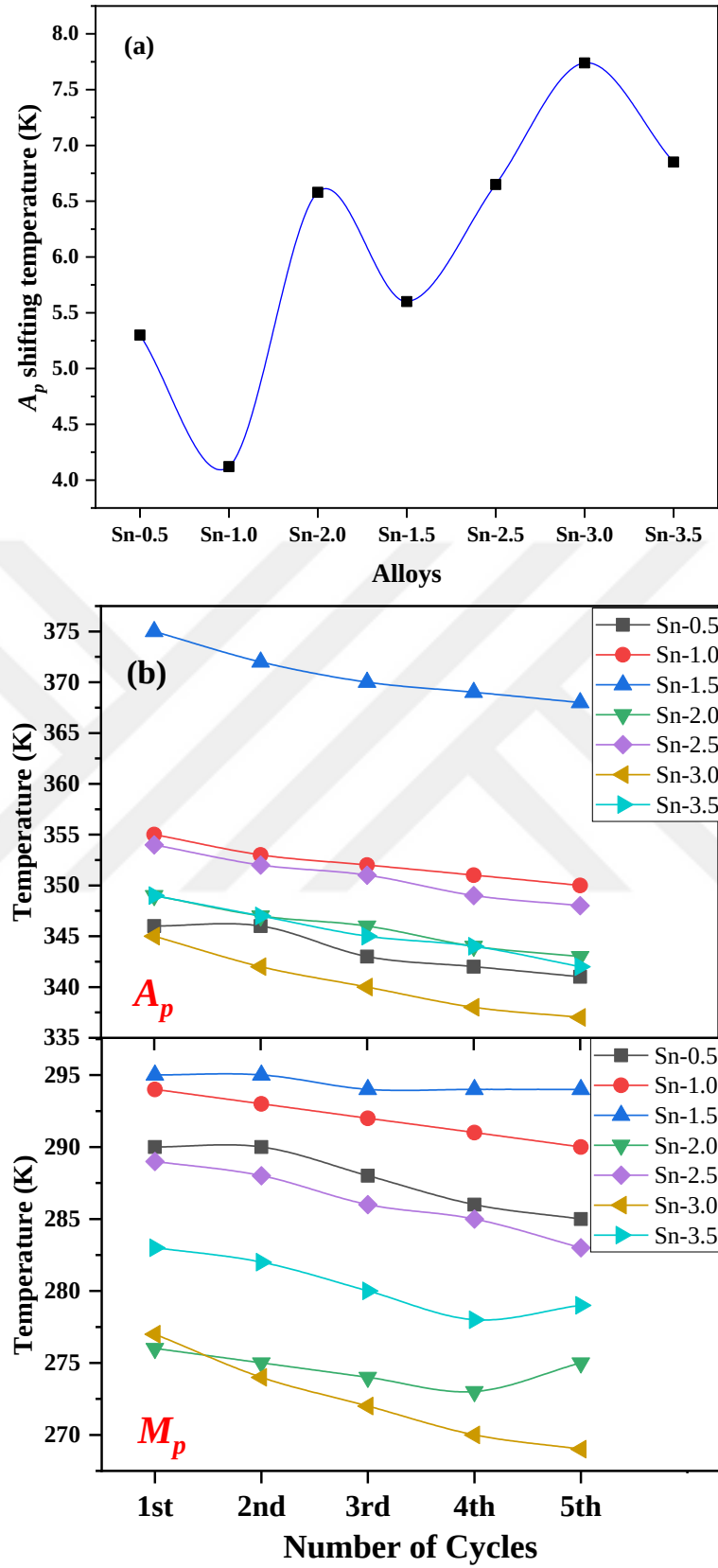


Figure 6.2. (a) Shifting austenite finish after completing five DSC cycling. (b) The value of austenite peak (top) and martensite peak (below) temperatures for each DSC cycle process of NiTiSn alloys

are solid phases with different crystal structures. Sometimes another shoulder appears before martensite and/ or austenite phase transformation that represents the intermediate phase, i.e., R-phase. The enthalpy change is demonstrated by ΔH with a superscript $A \rightarrow M$ (austenite $\rightarrow$ martensite) or $M \rightarrow A$ (martensite $\rightarrow$ austenite). The DSC results are plotted for heat flow against temperature, so the area under the trough and peaks simply gives the enthalpy change of the transformation process. The value of enthalpy change for both endothermic and exothermic process was found with the aid of the DSC software program (Perkin Elmer Sapphire), which based on the following formula [155]:

$$\Delta H^{M \rightarrow A} = \int_{A_s}^{A_f} \frac{dq}{dt} \left(\frac{dT}{dt} \right)^{-1} dT \quad \text{For martensite to austenite phase transformation} \quad (6.1a)$$

$$\Delta H^{A \rightarrow M} = \int_{M_s}^{M_f} \frac{dq}{dt} \left(\frac{dT}{dt} \right)^{-1} dT \quad \text{For austenite to martensite phase transformation} \quad (6.1b)$$

where q is the instantaneous heat absorbed (or expelled) by the SMA; T is the absolute temperature (in kelvin), and t is time. The values of $\Delta H^{M \rightarrow A}$ and $\Delta H^{A \rightarrow M}$ are listed in Table 6.1. Sn-1.5 alloy has recorded the most stable enthalpy changes for both forward and reverse phase transformations, while in the rest specimens (Sn-0.5, Sn-1.0, Sn-2.0, Sn-2.5, Sn-3.0, and Sn-3.5), the enthalpy change of the martensite phase transformation have generally diminished by increasing the number of non-isothermal DSC cycles.

The entropy change is always a positive value for the endothermic and exothermic processes and directly proportional to the enthalpy change of the phase transformation. The entropy change represents by ΔS with superscript $A \rightarrow M$ (austenite $\rightarrow$ martensite) or $M \rightarrow A$ (martensite $\rightarrow$ austenite). The entropy change of the martensitic phase transformation was found by the following equations [156]:

$$\Delta S^{A \rightarrow M} = T_o \Delta H^{A \rightarrow M} \quad \text{For martensite to austenite phase transformation} \quad (6.2a)$$

$$\Delta S^{M \rightarrow A} = T_o \Delta H^{M \rightarrow A} \quad \text{For austenite to martensite phase transformation} \quad (6.2b)$$

In Eq. (6.2a) and Eq. (6.2b), T_o is equilibrium temperature, and that temperature is determined where the Gibbs free energy for both austenite and martensite phase transformation is equal to zero. The value of equilibrium temperature can be determined by the average value of martensite start and austenite finish temperatures [157]:

$$T_o = 0.5(M_s + A_f) \quad (6.3)$$

The DSC cycling process linearly decreased the value of equilibrium temperature (Figure 6.3). Figure 6.4 shows the amount of $\Delta S^{A \rightarrow M}$ has been decreased after five complete cycles.

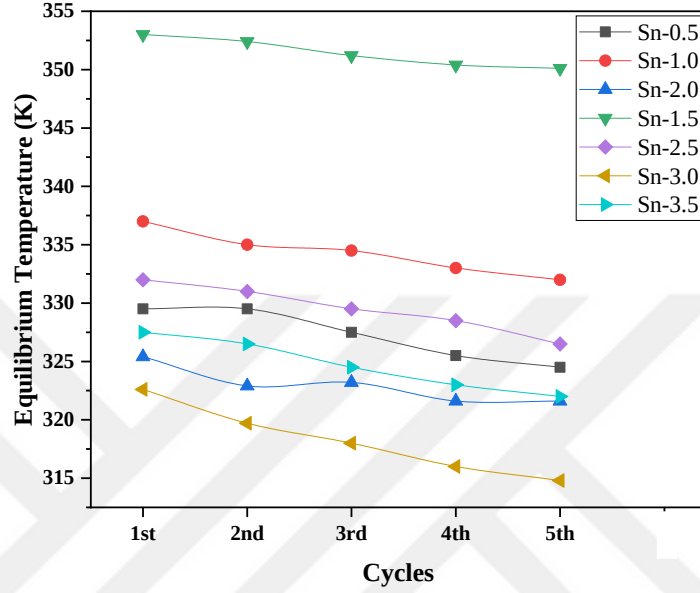


Figure 6.3. The value of equilibrium temperature for each DSC cycle of NiTiSn alloys

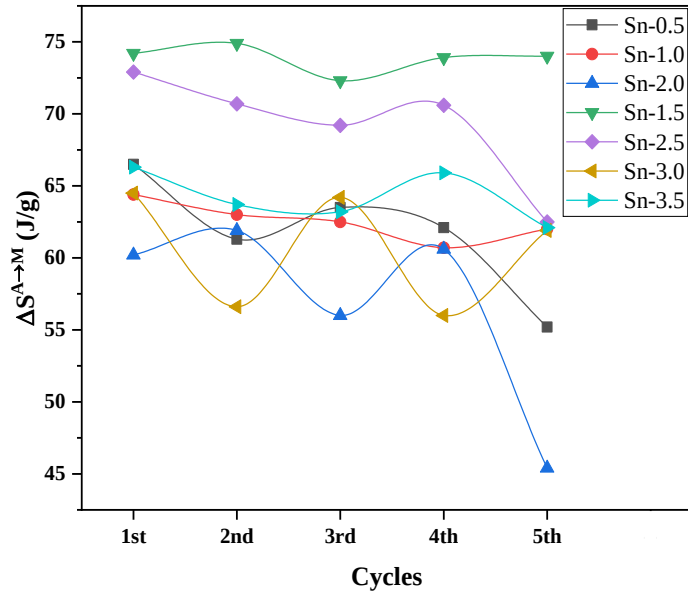


Figure 6.4. Entropy change of martensite phase transformation for NiTiSn alloys

As aforementioned, the equilibrium temperature is a temperature where the Gibbs free energy (ΔG) for forward and reverse phase transformation is zero, thus based on this definition the Gibbs free energy for austenite phase transformation can be formulated as [158]:

$$\begin{aligned}\Delta G^{M \rightarrow A}(T_o) &= G^A(T_o) - G^M(T_o) = (H^A - T_o S^A) - (H^M - T_o S^M) \\ &= \Delta H^{M \rightarrow A} - (T_o \Delta S^{M \rightarrow A}) = 0\end{aligned}\quad (6.4)$$

where G^A , H^A , and S^A represent Gibbs free energy, enthalpy, and entropy of the austenite phase; also, G^M , H^M , and S^M are the same parameters but with a superscript of M representing martensite phase. Gibbs free energy at martensite start and equilibrium temperatures can be used to achieve the Gibbs free energy of the martensite phase transformation:

$$\Delta G^{A \rightarrow M}(M_s) = \Delta G^{M \rightarrow A}(T_o) - \Delta G^{M \rightarrow A}(M_s) \quad (6.5)$$

Equation 6.5 can rearrange as follows [159-162]:

$$\Delta G^{A \rightarrow M}(M_s) = -(T_o - M_s) \Delta S^{M \rightarrow A} \quad (6.6)$$

The Gibbs free energy for martensite phase transformation can be calculated by using data available in Table 6.1 and the results obtained from Eq. (6.2b) and Eq (6.3). It can be seen that the value of $\Delta G^{A \rightarrow M}$ has generally increased by repeating the DSC cycling process on the alloys, excluding Sn-1.5, which has almost a constant value. Moreover, the elastic energy deposited in the martensite variants can be calculated using the following equation [163-166]:

$$G_E = \Delta G^{A \rightarrow M}(M_s) - \Delta G^{A \rightarrow M}(M_f) = (M_s - M_f) \Delta S^{M \rightarrow A} \quad (6.7)$$

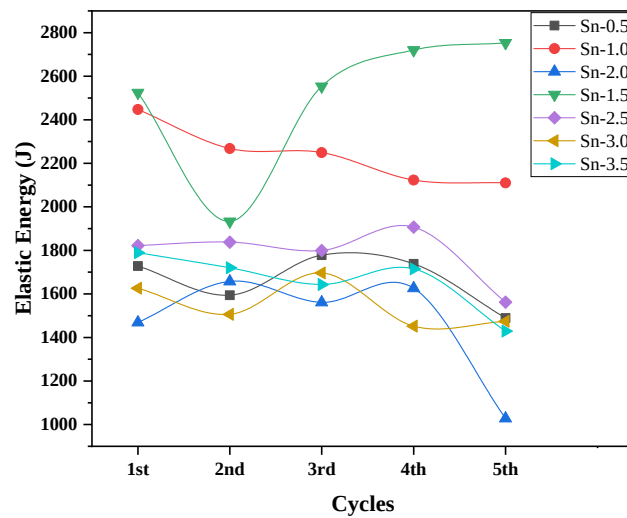


Figure 6.5. The elastic energy of the NiTiSn alloys

Figure 6.5 illustrates elastic energy against the number of DSC cycles. The value of G_E has different statuses, for example, its value increases with increasing the number of DSC cycling in the Sn-1.5 alloy, while its value unlikely decreased in the rest of the specimens. The capacity for restoring energy has been reduced by decreasing elastic energy. Elastic energy values of Sn-0.5 and Sn-3.5 have approximately the same pattern.

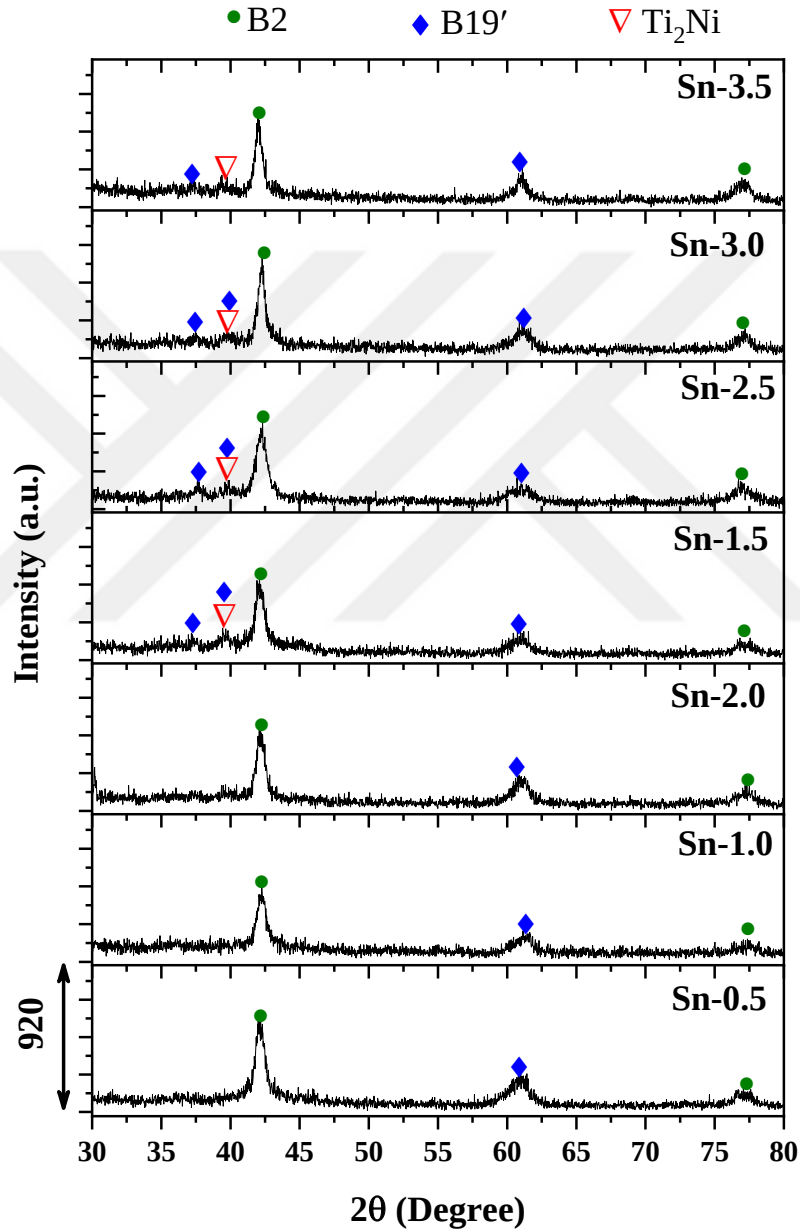


Figure 6.6. XRD patterns of all samples.

Figure 6.6 illustrates the X-ray diffraction pattern of the NiTiSn-ingot alloys. The peaks were indexed by sources available in the literature [31, 32, 36, 53, 167, 168]. Three various phases were found in the alloys, including the matrix and the secondary phases (Ti_2Ni and Ti_3Sn). The X-ray

diffraction measurements were carried out at room temperature, which is located between austenite and martensite phase transformations (see DSC results, Figure 6.1), so the main phase of the alloys cannot be completely transformed. The main peaks are the austenite phase (B2), and the martensite phase (B19') represents the minority phase compared to the austenite phase. It is worth knowing that B2 is a body-centered cubic with a high similarity crystal structure compared to the B19' (monoclinic crystal structure) and Ti₂Ni (face centered cubic crystal structure) [169, 170].

It is proved that the Ti₃Ni₄ phase in the NiTi-based alloys is responsible to produce a two-step martensitic phase transformation and the precipitate phase is produced during the aging process in temperatures between 600-800K [171, 172]. In Figure 6.1c and Figure 6.1d (the DSC results), shoulder peaks were observed during the cooling process, while the two-stepped phase transformation for Sn-2.5, Sn-3.0, and Sn-3.5 alloys has not been detected. The NiTiSn-ingot SMAs have not experienced the annealing process and the characterization has been accomplished after casting.

The crystallite size (*D*) of the NiTiSn-ingot SMAs can be anticipated indirectly by using the X-ray diffraction results. Debye Scherrer equation is a typical model that is popularly used for finding nano-crystallite with the aid of XRD analysis. Some quantities that can be found from the XRD analysis are the full width at half maximum (FWHM) represented by *B*, the wavelength of the X-ray (*λ*) used for scanning the samples, and the angle (*θ*) that should be in radian. The Debye Scherrer Equation is given as [14, 173, 174]:

$$D = K \lambda / (B \cos \theta) \quad (6.8)$$

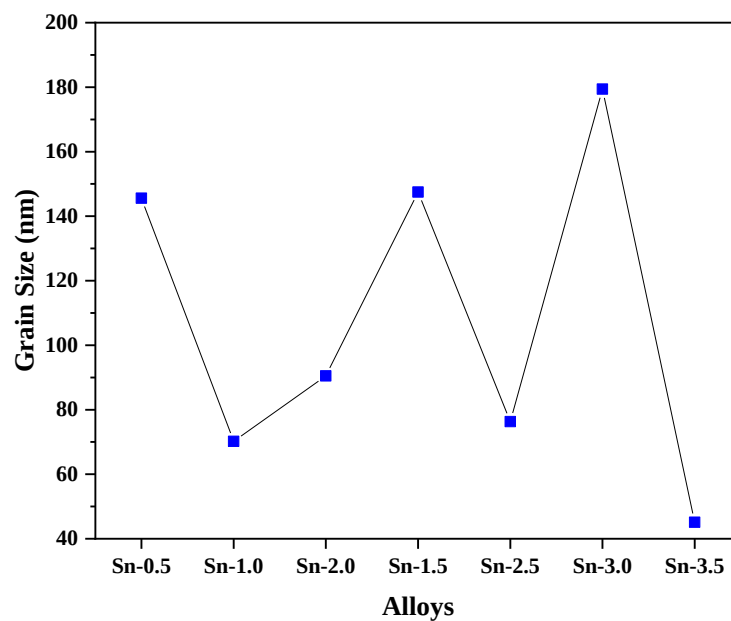


Figure 6.7. The grain size (or crystallite size) of the NiTiSn shape memory alloys

where Scherrer's constant (K) is assumed as a constant value (0.9), also the output of the X-ray source was filtered and only a monochromatic wavelength was used, which is $\text{Cu } K_{\alpha}$ X-ray with $\lambda (=1.5406\text{\AA})$. The average value of crystallite size is presented in Figure 6.7. In all specimens, the crystallite size is less than 200 nm, which is difficult to be observed using a scanning electron microscope. The size of crystallites impacts on different properties of the alloys, e.g., hardness.

Figure 6.8 displays the measured Vickers microhardness of the NiTiSn-ingot SMAs. The test was accomplished for both matrix (main phase) and the second phase (Ti_2Ni). It is clear that the matrix phase of Sn-0.5 alloy has recorded a higher microhardness value compared with the rest of the samples. Additionally, the Vickers microhardness and crystallite size values of the second phase have a similar pattern, i.e., these quantities correlated to each other. Our results are supported by Krishna [175] and Xia [176] studies. They reported that the microhardness of NiTi alloy increases with increasing the size of the nanocrystallites.

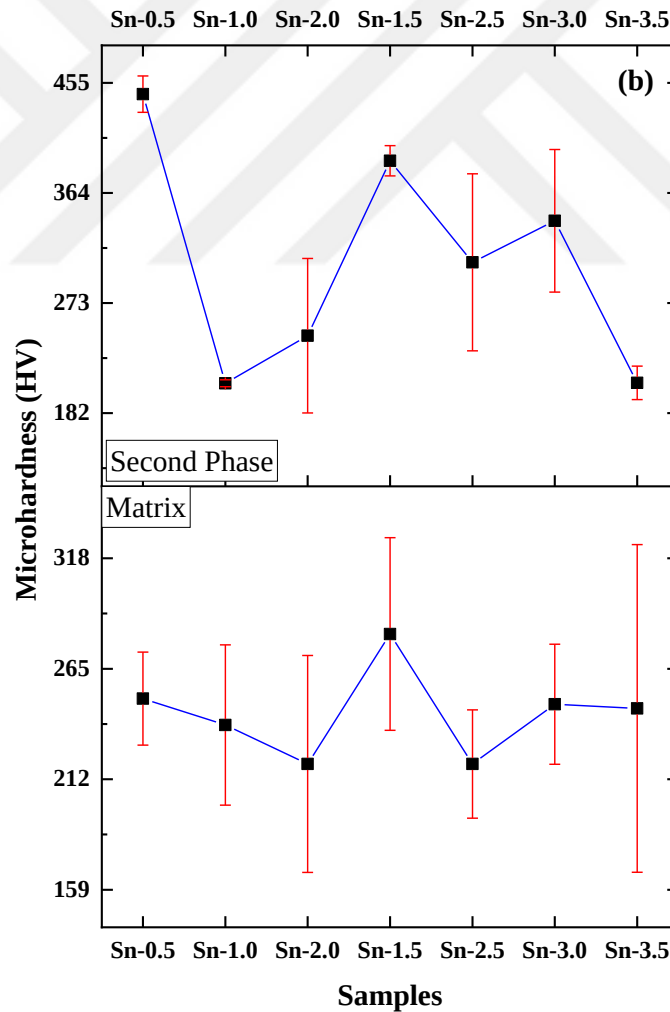


Figure 6.8. Microhardness results for matrix and second phase of the NiTiSn alloys

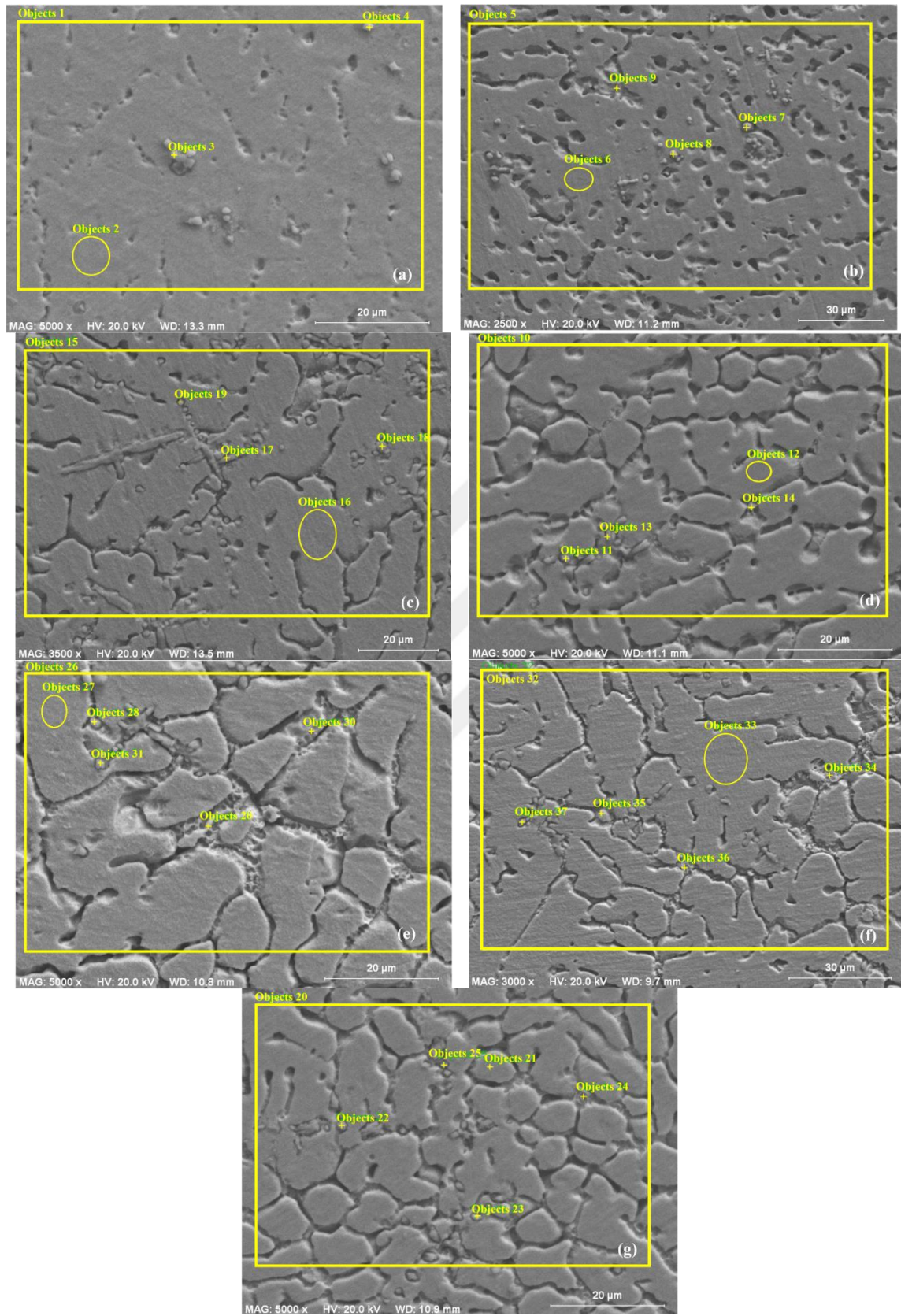


Figure 6.9. SEM images of all specimens, (a) Sn-0.5, (b) Sn-1.0, (c) Sn-2.0, (d) Sn-1.5, (e) Sn-2.5, (f) Sn-3.0, and (g) Sn-3.5

Table 6.2. Chemical composition results of Sn0.5, Sn1.0, Sn1.5, Sn2.0, Sn2.5, Sn3.0, and Sn3.5 alloys for matrixes and various microstructures determined on the SEM images

Alloys code	Spectrum no	Ni (%at.)	Ti (%at.)	Sn (%at.)	phases
Sn-0.5	1	48.62	50.68	0.70	NiTi(B2)
	2	49.43	49.98	0.59	NiTi(B2)
	3	29.06	70.25	0.69	Ti ₂ Ni
	4	48.03	51.19	0.77	NiTi(B2)
Sn-1.0	5	48.68	50.48	0.84	NiTi(B2)
	6	49.03	50.46	0.52	NiTi(B2)
	7	18.01	81.78	0.21	Ti-rich
	8	39.50	60.03	0.48	Ti ₃ Ni ₂
	9	48.87	50.36	0.77	NiTi(B2)
Sn-2.0	15	46.78	52.16	1.05	NiTi(B2)
	16	49.02	49.68	1.30	NiTi(B2)
	17	23.01	76.33	0.66	Ti ₂ Ni
	18	7.09	92.52	0.39	Ti-rich
	19	32.19	64.79	3.02	Ti ₂ Ni
Sn-1.5	10	47.76	51.00	1.24	NiTi(B2)
	11	44.69	54.57	0.74	NiTi(B2)
	12	49.38	49.84	0.79	NiTi(B2)
	13	48.92	50.42	0.66	NiTi(B2)
	14	47.82	50.42	1.77	NiTi(B2)
Sn-2.5	26	47.46	50.93	1.61	NiTi(B2)
	27	49.64	49.58	0.78	NiTi(B2)
	28	15.59	83.83	0.57	Ti-rich
	29	47.94	49.72	2.34	NiTi(B2)
	30	49.22	49.66	1.11	NiTi(B2)
	31	12.52	86.95	0.53	Ti-rich
Sn-3.0	32	48.28	49.94	1.78	NiTi(B2)
	33	49.62	49.34	1.04	NiTi(B2)
	34	37.86	54.88	7.27	Ti ₂ Ni
	35	28.93	59.67	11.39	Ti ₂ Ni
	36	37.46	54.55	7.98	Ti ₂ Ni
	37	44.57	54.21	1.22	NiTi
Sn-3.5	20	46.14	51.73	2.13	NiTi(B2)
	21	49.40	49.35	1.25	NiTi(B2)
	22	17.44	81.67	0.89	Ti-rich
	23	18.05	80.88	1.07	Ti-rich
	24	33.10	57.63	9.27	Ti ₂ Ni
	25	34.36	59.65	5.98	Ti ₂ Ni

The microstructural analysis showed that the amount of Sn in the NiTiSn alloy affects the shape and size of microstructures. Figure 6.9 demonstrates the SEM images and the composition of some selected areas and spots that have been shown with yellow color. The EDX results give the composition ratio of the aforementioned determined areas on the SEM images (Table 6.2). The austenite (B2) phase is the dominant matrixes phase with a low fraction of martensite (B19') phase. Also, some precipitation can be seen, which their species and the quantities various for different specimens. Additionally, in this compositional analysis, no Sn has not detected in the matrix structure; accordingly, it can be assumed that Sn could be totally dissolved in the alloys. Some

SEM images showed some fragmentation on the surface of the alloys, and this fragmentation growth by the rise of Sn content; moreover, some sphere-like Ti-rich phases were growth in the grooves.

Figure 6.10 demonstrates the concentration of the constituents of Sn-0.5 and Sn-3.5 alloys. Almost identical elements are scattered in the Sn-0.5 alloy, while in the boundaries, Ti-rich and the dissolved-Sn elements have increased by decreasing Ni elements, which could be the only reason behind growing fragmentations in the NiTiSn-ingot alloy.

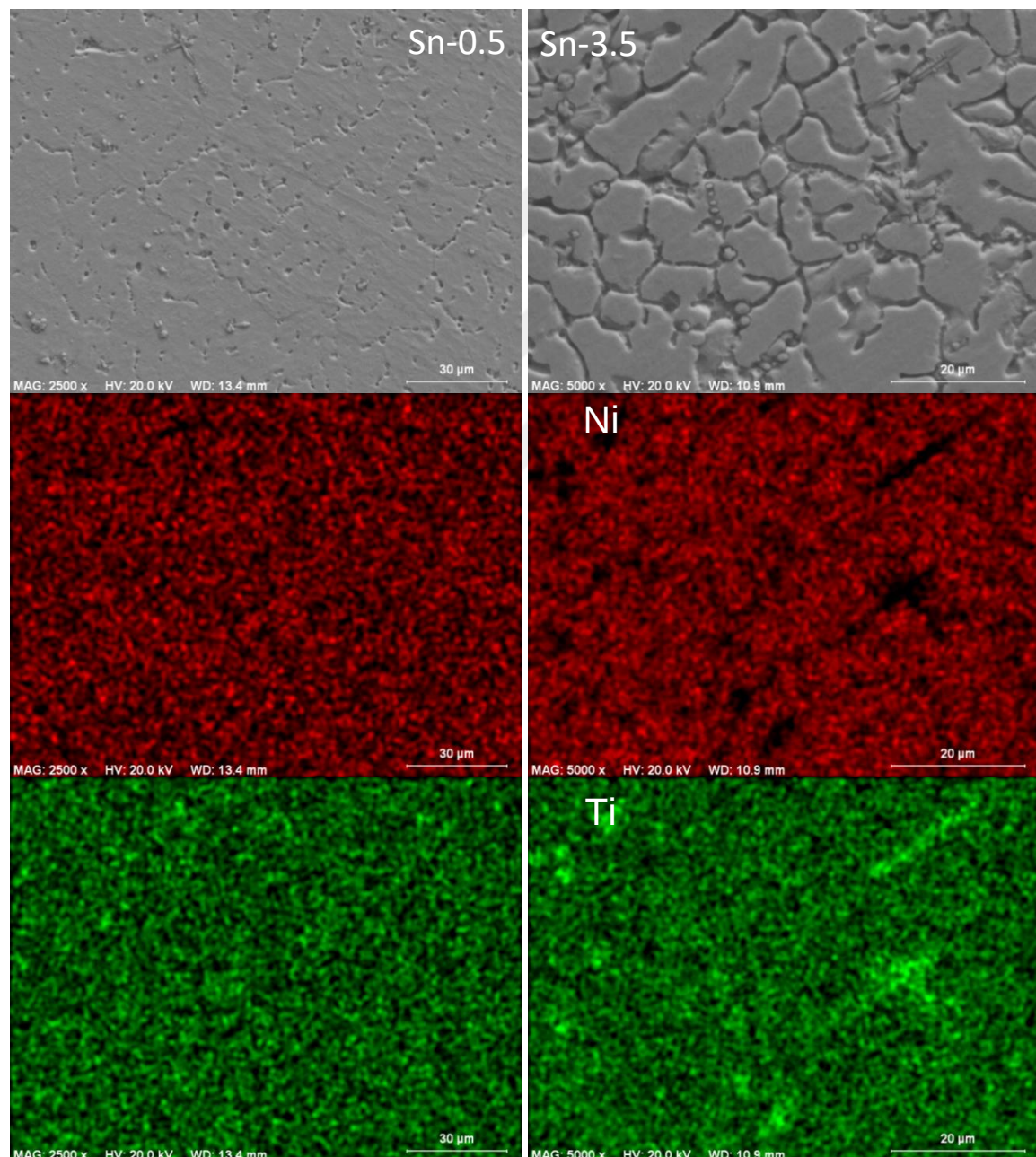


Figure 6.10. Mapping of Sn-0.5 and Sn-3.5 alloys, where red, green, and blue represents Ni, Ti, and Sn element, respectively

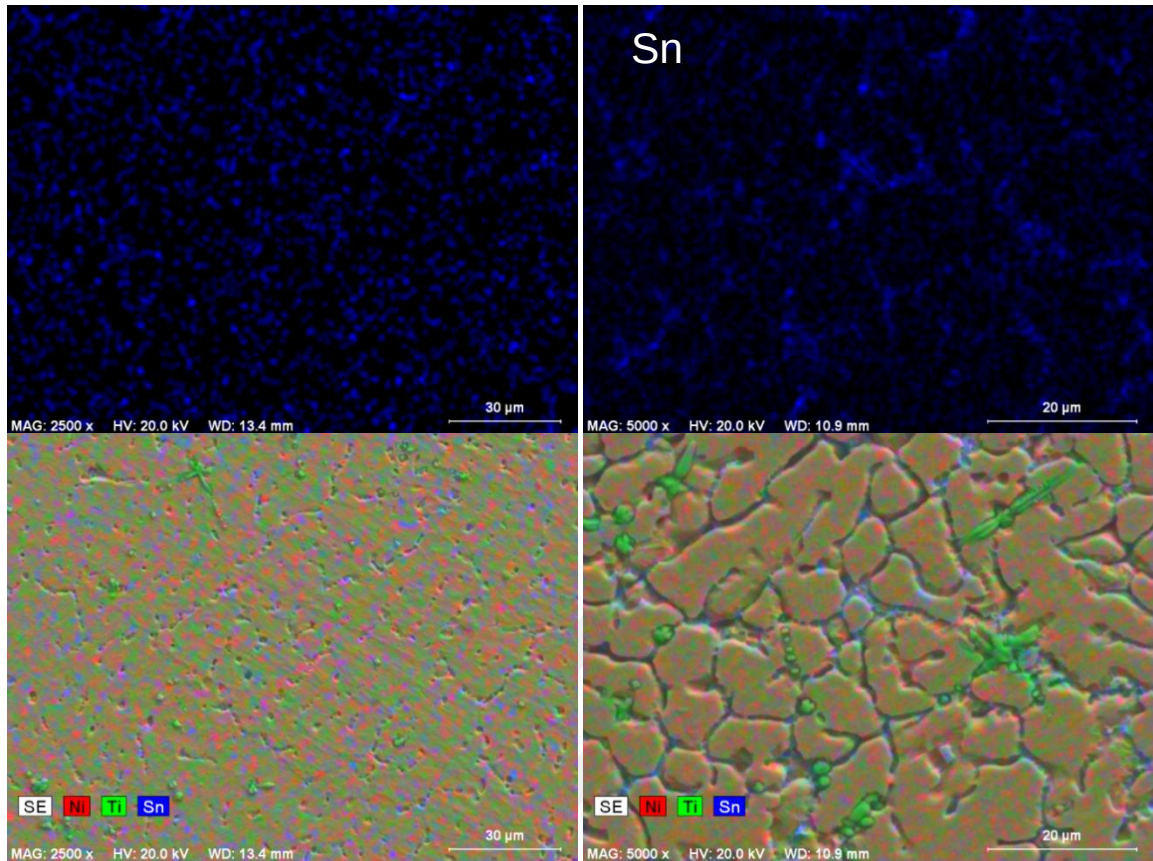


Figure 6.10. Mapping of Sn-0.5 and Sn-3.5 alloys, where red, green, and blue represents Ni, Ti, and Sn element, respectively (continue)

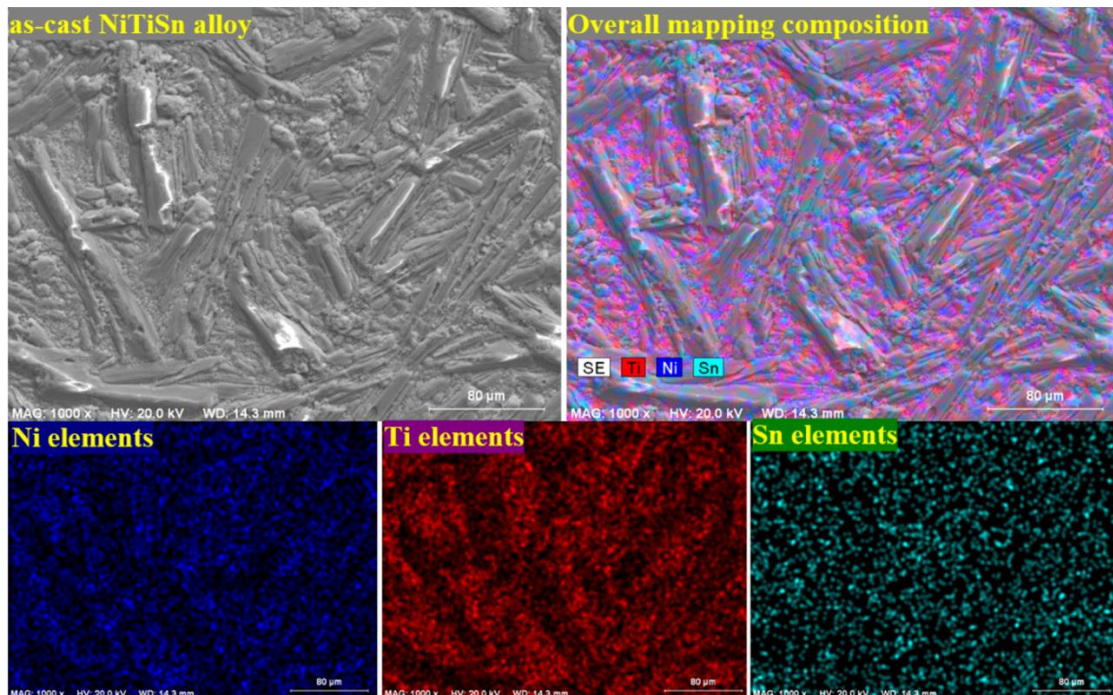


Figure 6.11. Mapping composition of the as-cast NiTiSn alloy

6.2. Wire-Shaped NiTiSn SMA

The map of all constituents of the as-cast NiTiSn-wire SMA is displayed in Figure 6.11. The Ni, Ti, and Sn elements are demonstrated in blue, red, and green, respectively. The dark color in the background of each map indicates the residual elements excluding the corresponding element. The alloy looks homogenous and the elements were mixed well. Therefore, it can be assumed that the as-cast samples, which cut from the alloy, have the same physical properties.

Five cycles of DSC measurements of the as-casted NiTiSn-wire SMA are shown in Figure 6.12. In both heating and cooling processes, the DSC curves have a shoulder before austenite and martensite phase transformations. These two-step phase transformations can be expressed as (martensite phase $\rightarrow$ R-phase $\rightarrow$ austenite phase) and (austenite phase $\rightarrow$ R-phase $\rightarrow$ martensite phase) for reverse and forward process. The [martensite phase $\rightarrow$ R-phase]-peak is diminished over the DSC cycle operations, whereas the [austenite phase $\rightarrow$ R-phase]-peak in the forward process is grown and the peak has distanced from [R-phase $\rightarrow$ martensite phase]-peak. Moreover, the peak of austenite and martensite phase transformations have shifted around 7.76 and 8.7 K to the lower temperature. Likewise, Wang et al. reported a nearly similar shift for a Ni-rich NiTi alloy [177].

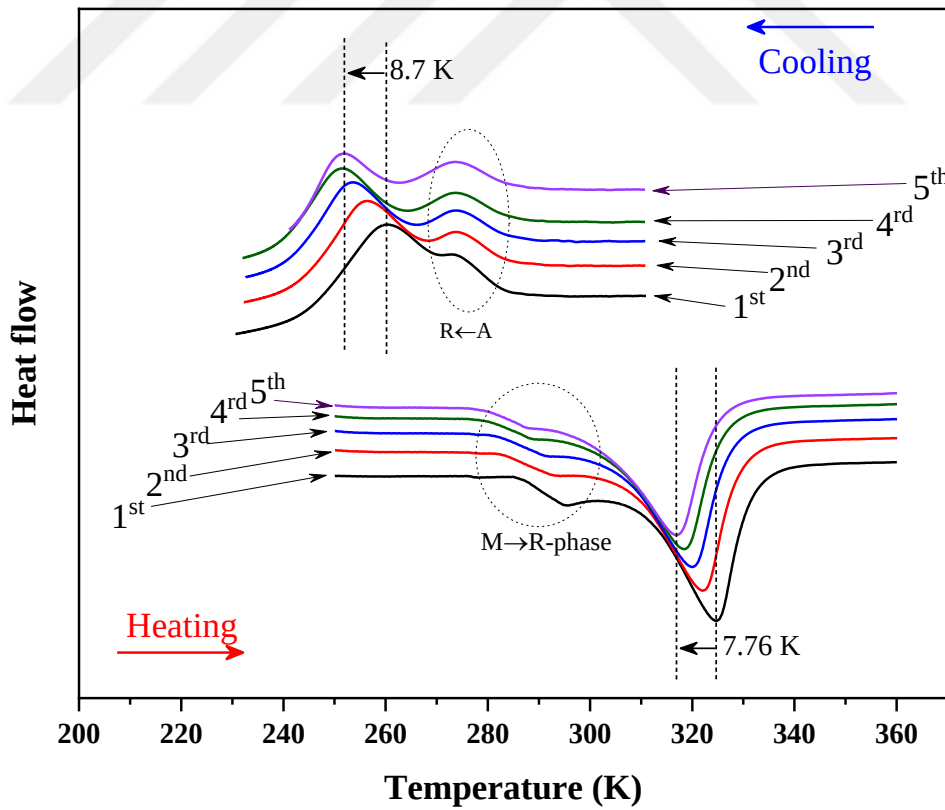


Figure 6.12. The DSC results of the as-cast NiTiSn alloy wire

The NiTiSn-wire SMA had a cylindrical shape and it is immersed with only one end inside the electrolyte. Therefore, the area of the sample was found as follows:

$$\text{Surface area of the cylinder } (A_s) = 2\pi rh \quad (6.9)$$

$$\text{Area of the cylinder's base } (A_b) = \pi r^2 \quad (6.10)$$

$$\text{Total area of our sample } (A_t) = A_s + A_b = 2\pi rh + \pi r^2 \quad (6.11)$$

where π is an irrational value (≈ 3.14), r is the radius, and h is the height of the sample immersed in the electrolyte solution. The value of r , h , and A_t is listed in Table 6.3.

Table 6.3. The value of the radius, height, and area of the NiTiSn-wire alloy used for corrosion test

r (m)	h (m)	A_s (m ²)	A_b (m ²)	A_t (m ²)
1.5×10^{-3}	12×10^{-3}	113.10×10^{-6}	7.07×10^{-6}	120.17×10^{-6}

The electrochemical Tafel polarization in both solutions (SBF and PS) at room temperature and body temperature was carried out. Figure 6.13a and Figure 6.13b demonstrate the Tafel electrograms of the as-cast NiTiSn-wire SMA in SBF and PS solutions. For the x-axis, the corrosion current was divided by the area of samples that interacted with solutions, and for the y-axis, the

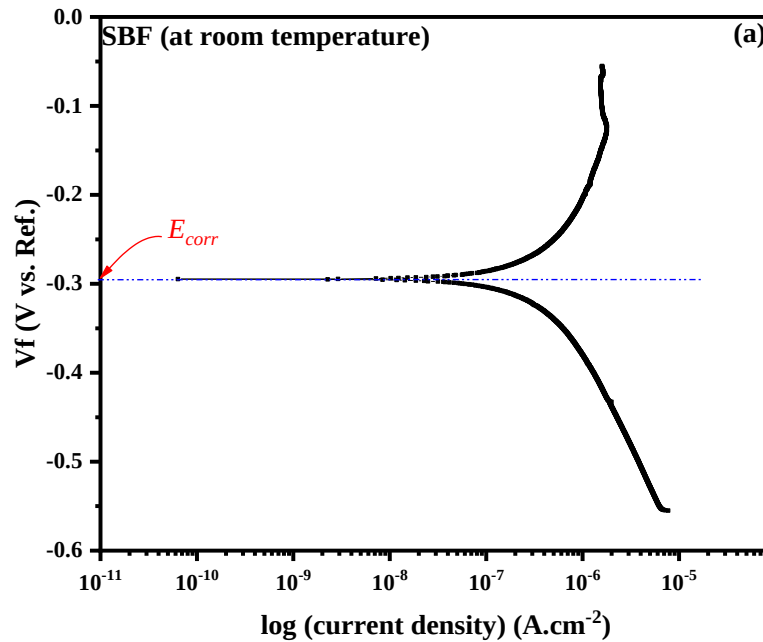


Figure 6.13. Obtaining (a) potential corrosion, (b) corrosion current, and (c) anodic and cathodic Tafel slopes

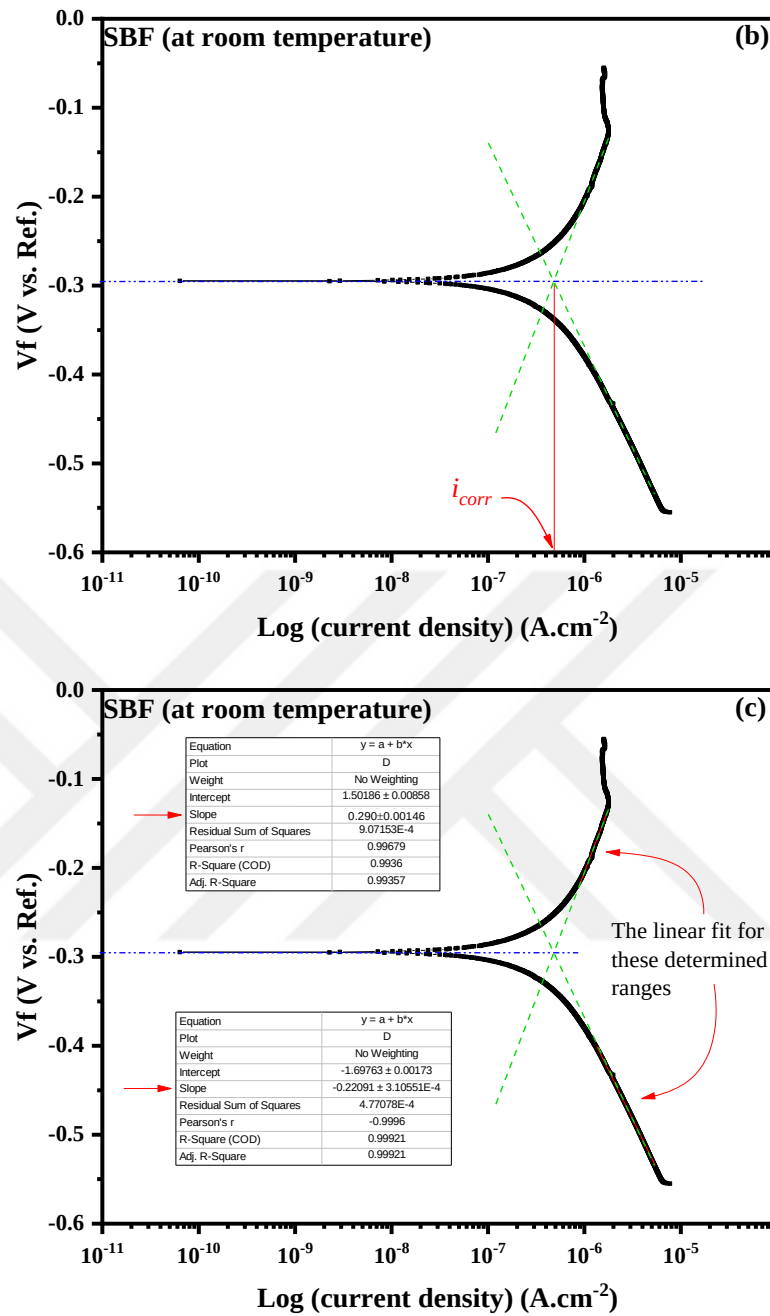


Figure 6.13. Obtaining (a) potential corrosion, (b) corrosion current, and (c) anodic and cathodic Tafel slopes (continue)

measured potential of the sample with respect to the reference electrode was used. Corrosion Current density (i_{corr}) and Corrosion Rate (CR) represents the amount of material lost throughout the corrosion process. The analyzed result gives some valuable quantities, including corrosion potential (E_{corr}), corrosion current density (i_{corr}), breakdown potential (E_b), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), corrosion rate (CR), and potential resistance (R_p).

For example, we found E_{corr} at the intercept, where the anodic and cathodic changes in the logarithmic x-axis sharply change. The horizontal blue line (dot-dot- dashed line style) in Figure 6.13a represents the E_{corr} of the alloy measured in SBF at room temperature. The green line (dot-dashed line) represents the intercept of two straight lines drawn from tangential anodic and cathodic curves. The intercept of the straight lines should cross the E_{corr} (the blue horizontal line). The corrosion current was obtained by Tafel extrapolation analysis (Tafel fit). The current at the determined point represents corrosion current (i_{corr}). Basically, the slope of cathodic (β_c) and anodic (β_a) Tafel can be obtained for two points in the tangential lines. In this study, we found the Tafel slopes using a linear fit for a particular range of data (almost located on the drawn green lines) using the OriginLab program (Figure 6.13c). The value of the electrochemical parameters, including E_{corr} , i_{corr} , β_c , and β_a , are listed in Table 6.4.

Table 6.4. Electrochemical polarization parameters of the as-cast NiTiSn-wire shape memory alloy in Simulated Body Fluid (SBF) and Physiological Solution (PS), (Reference electrode, Ag/AgCl)

Sample	E_{corr} (V)	β_a (V)	β_c (V)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	CR (mmpy)	R_p ($\text{k}\Omega\cdot\text{cm}^2$)	Medium
At room temperature	-0.295	0.290	0.221	0.486	0.22×10^{-4}	112.1	SBF
	-0.177	0.124	0.197	0.914	0.41×10^{-4}	36.2	PS
At body temperature	-0.172	0.178	0.118	0.105	4.66×10^{-4}	294.1	SBF
	-0.158	0.218	0.093	0.172	7.63×10^{-4}	164.6	PS

Figure 6.14 illustrates all electrochemical parameters achieved from Tafel graphs and related calculations. E_{corr} values have a much positive shift in body temperature compared to room temperature, and in both temperatures, E_{corr} of the sample has more shifted to the cathodic direction in the SBF (Figure 6.14a). Current density and hence i_{corr} decreased in BT compared to RT, and i_{corr} has recorded a lower value in SBF compared to SP (Figure 6.14b). The cathodic Tafel slopes (β_c) is decreased with increasing temperature from RT to BT in both solutions (Figure 6.14c). Also, the anodic Tafel slope is diminished with increasing temperature in SBF, while in PS the β_a is increased by increasing temperature (Figure 6.14d). The corrosion rate (CR) for one year was calculated by the following equation [178]:

$$CR\left(\frac{mm}{year}\right) = 0.13 \times i_{corr} \left(\frac{e}{\rho}\right) \quad (6.12)$$

where e is equivalent weight, ρ is the mass density. A sharp increase of CR can be seen for the NiTiSn-wire alloy at BT compared to RT (Figure 6.14e). The CR can be affected by the type, the

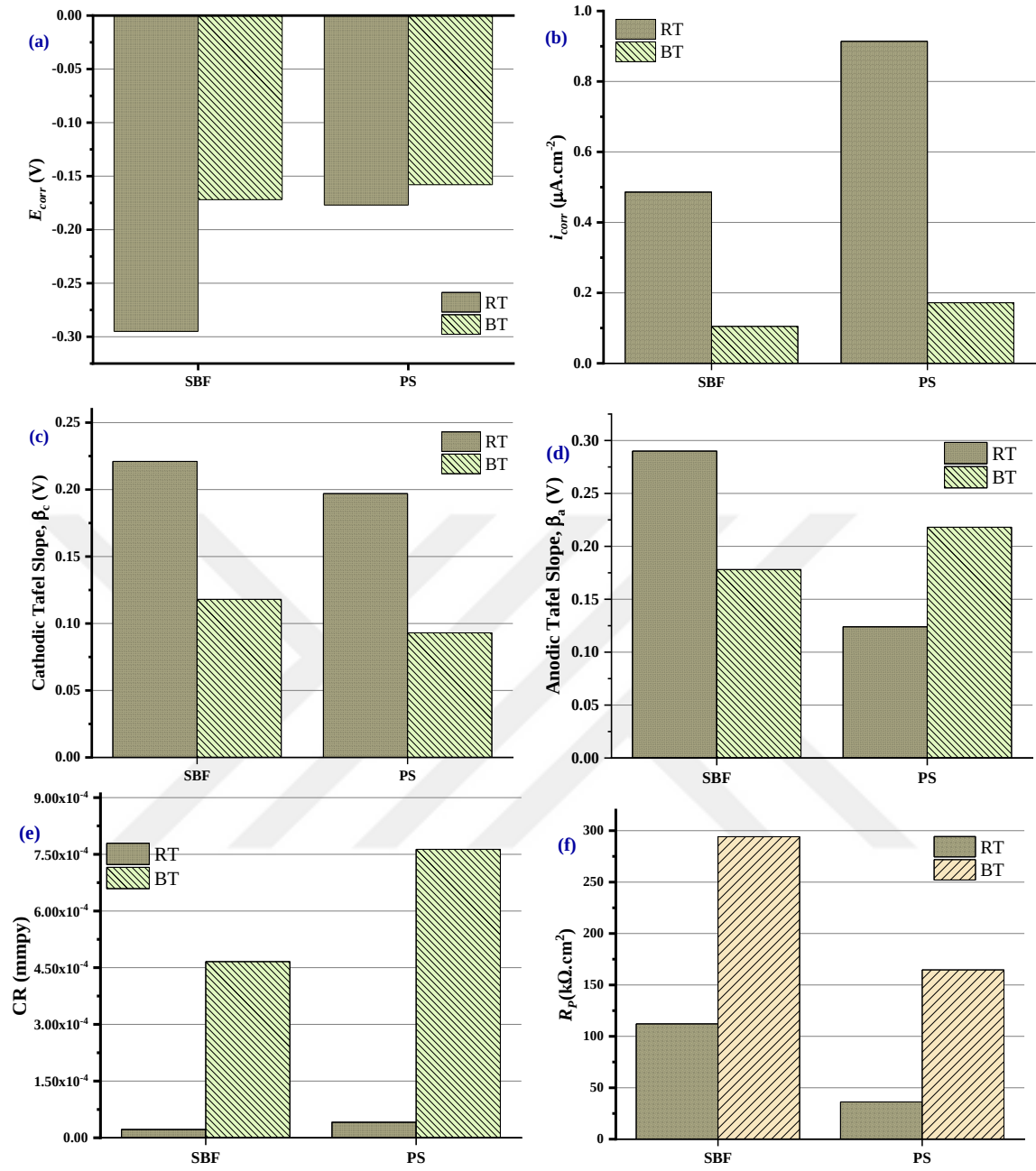


Figure 6.14. Electrochemical polarization parameters for the as-cast NiTiSn-wire shape memory alloy in Simulated Body Fluid (SBF) and Physiological Solution (PS), (Reference electrode, Ag/AgCl). (a) E_{corr} , (b) j_{corr} , (c) β_c , (d) β_a , (e) CR, and (f) R_p

surface protection [179], pH of electrolyte, and temperature [180]. Wang et al. studied the impact of pH, temperature and Cl^- concentration on corrosion properties of a binary NiTi SMA. They stated that the pitting potential of the alloy in artificial saliva diminished at low and high pH, moreover, by increasing chloride (Cl^-) concentration, the pitting potential was decreased. In addition, they have changed the temperature to investigate the effect of corrosion on different phases. They found that the E_{corr} of austenite phase had lower value compared to the combination of both austenite and martensite phase [180]. The value of the corrosion rate as a function of

temperature can be seen in Table 6.4. The obtained CR value of the NiTiSn in SBF is $4.81 \cdot 10^{-4}$ mmpy, which is less than $7.86 \cdot 10^{-4}$ mmpy found for PS at BT. It is found that the corrosion rate of the NiTiSn is enhanced compared to binary NiTi alloys [181-183], thus it can be stated that adding Sn into NiTi alloys could rise the corrosion resistance of the alloy in both electrolytes. The key goal of this study was to reveal how the anti-corrosion performance, and hence biocompatibility of the NiTi-based SMAs can be improved by alloying with Sn additive.

The polarization resistance (R_p) for both solutions was calculated using the following equation [184]:

$$R_p = \frac{\beta_c \times \beta_a}{2.303 \times i_{corr} \times (\beta_c + \beta_a)} \quad (6.13)$$

The R_p of the as-cast NiTiSn SMA was calculated using Eq. 6.13. Figure 6.14f reveals the value of R_p for different environmental solutions and different temperatures. The alloy recorded higher R_p in SBF compared to PS and the R_p value even further increased by increasing the temperature from RT to BT. Having high R_p is an advantage for biomedical implantation applications. Yan et al. found that R_p value for a laser-welded NiTi alloy in 0.9% NaCl solution is around $100 \text{ k}\Omega \cdot \text{cm}^{-1}$ [185]. The obtained result for the arc-melted NiTiSn-wire SMA in SBF is higher, which showed that the alloy has sufficient biocompatibility.

Tafel polarization for both solutions at RT and BT is shown in Figure 6.15. In all cases, an active to passive transition can be seen. Normally, a passive film is produced on the alloy during anodic Tafel measurement. For NiTi-based alloys, mostly the film is a TiO_2 [186], furthermore, a small fraction of TiO , Ti_2O_3 , and Ni_2O_3 was detected [187-189]. Titanium has lower nucleation energy compared to the other constituents that are why TiO_2 dominates the passive film [190].

We investigated the oxidation behavior and some related oxidation parameters for the NiTiSn-wire shape memory alloy. First of all, a small piece of the alloy was subjected to a non-oxidation process from room temperature (300K) to (1300K) in natural air. Wang et al. reported that for an equiatomic-NiTi SMA, a Ni-free oxide film was produced on its surface for temperatures above 773 K [191]. Figure 6.16a reveals the mass change as a function of temperature. It can be seen that the alloy showed four different oxidation behaviors. Initially, the mass of the alloy stays constant, i.e., there was not enough energy for the nucleation of the oxide film. The oxidation started right at 853K and increased by increasing temperature. The mass gain from 1223K to 1498K is the same, then it noticeably changed between 1223K and 1498K and it has a sharp increase after 1498K.

We cut three small pieces from the as-cast NiTiSn-wire SMA, then they were subjected to a temperature of 853K, 1223K, and 1498K, isothermally. Figure 6.16b displays the isothermal

oxidation behavior of the NiTiSn-wire specimens. The oxidation constant (k_p) for the specimens was calculated by [192, 193]:

$$(\Delta W/A)^2 = k_p t \quad (6.14)$$

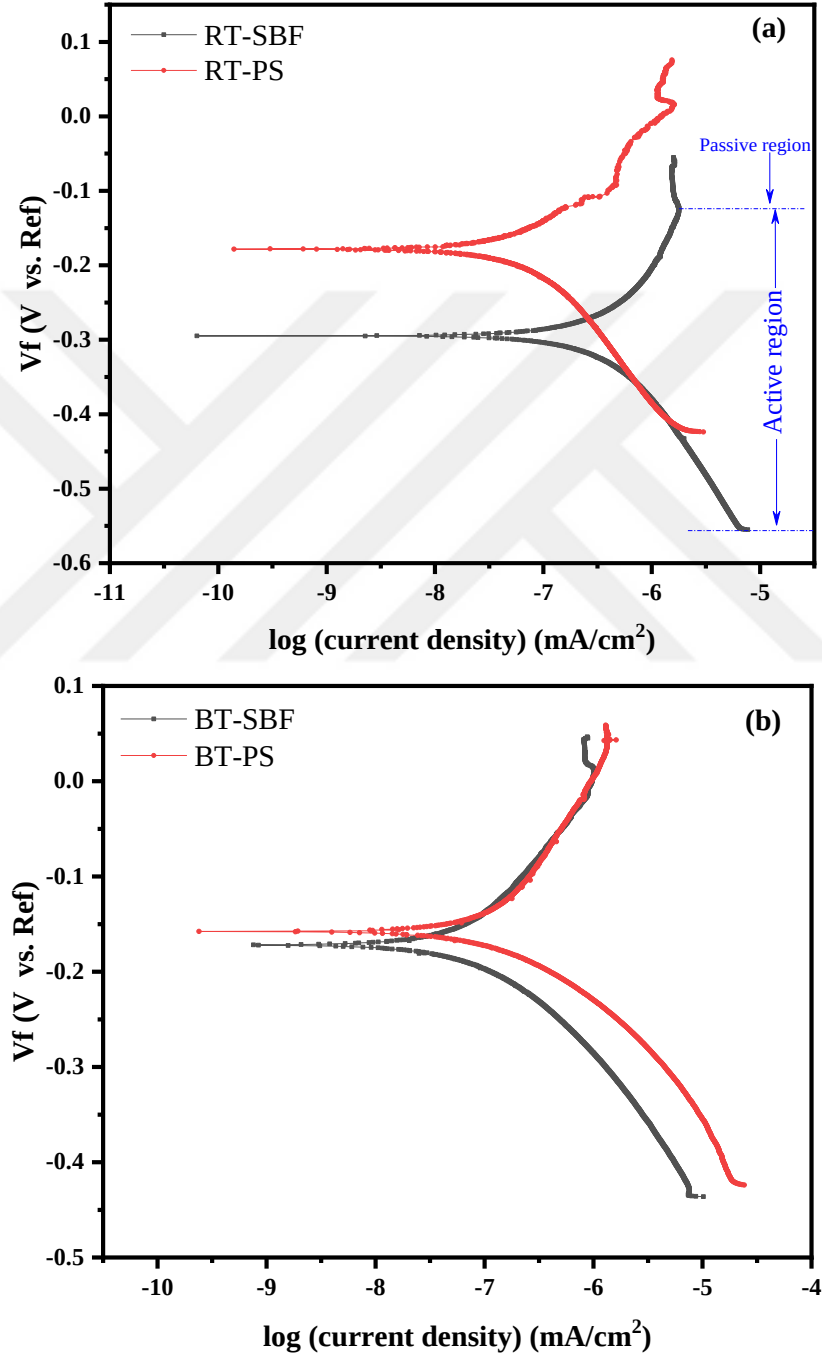


Figure 6.15. Electrical corrosively of the as-cast alloys obtained (a) at room temperature and (b) body temperature in both SBF and PS

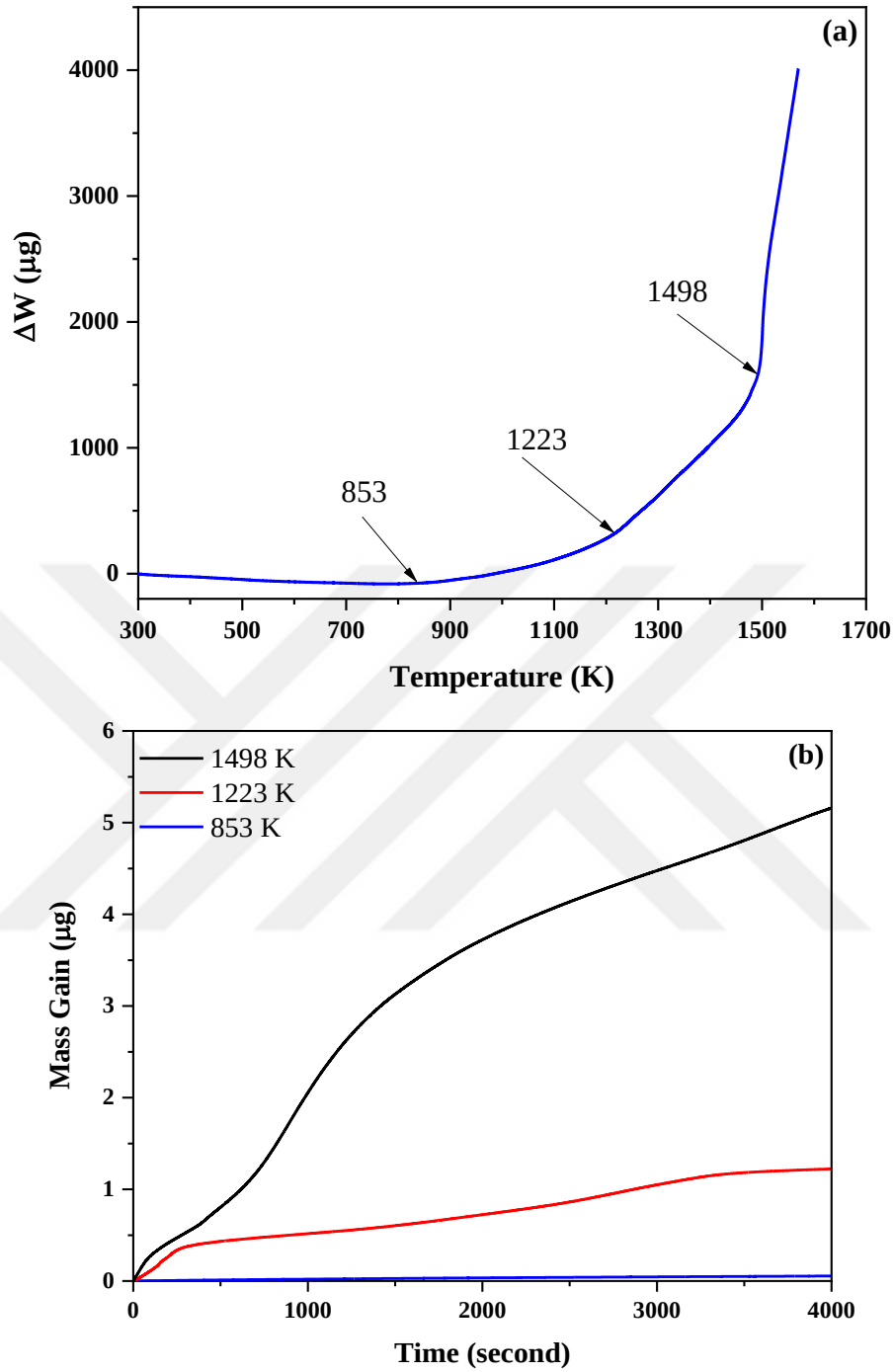


Figure 6.16. (a) Thermal and (b) isothermal mass gain curves of the NiTiSn alloys

where t represents the time, ΔW is the change in mass, A is the surface area of the sample, and $\Delta W/A$ represents the mass gain per unit area. The value of k_p was obtained from the slope of the linear fit of $(\Delta W/A)^2$ vs. time (sec). Table 6.5 lists the value of k_p and correlation constants (R^2). The closer the R^2 approaches one, the more accuracy the higher the fitting curve, and hence, properly obtaining the slope (k_p). Additionally, the results satisfy the parabolic law [192].

Table 6.5. Oxidation constants of the NiTiSn-wire alloys

Samples	Oxidation Constant (K_p) ($\text{mg}^2/\text{mm}^4\text{s}^{-1}$)	Correlation constant (R^2)
As-cast	----	----
Oxide-853K	1.68×10^{-8}	0.99
Oxide-1223K	7.44×10^{-6}	0.97
Oxide-1498K	1.41×10^{-4}	0.99

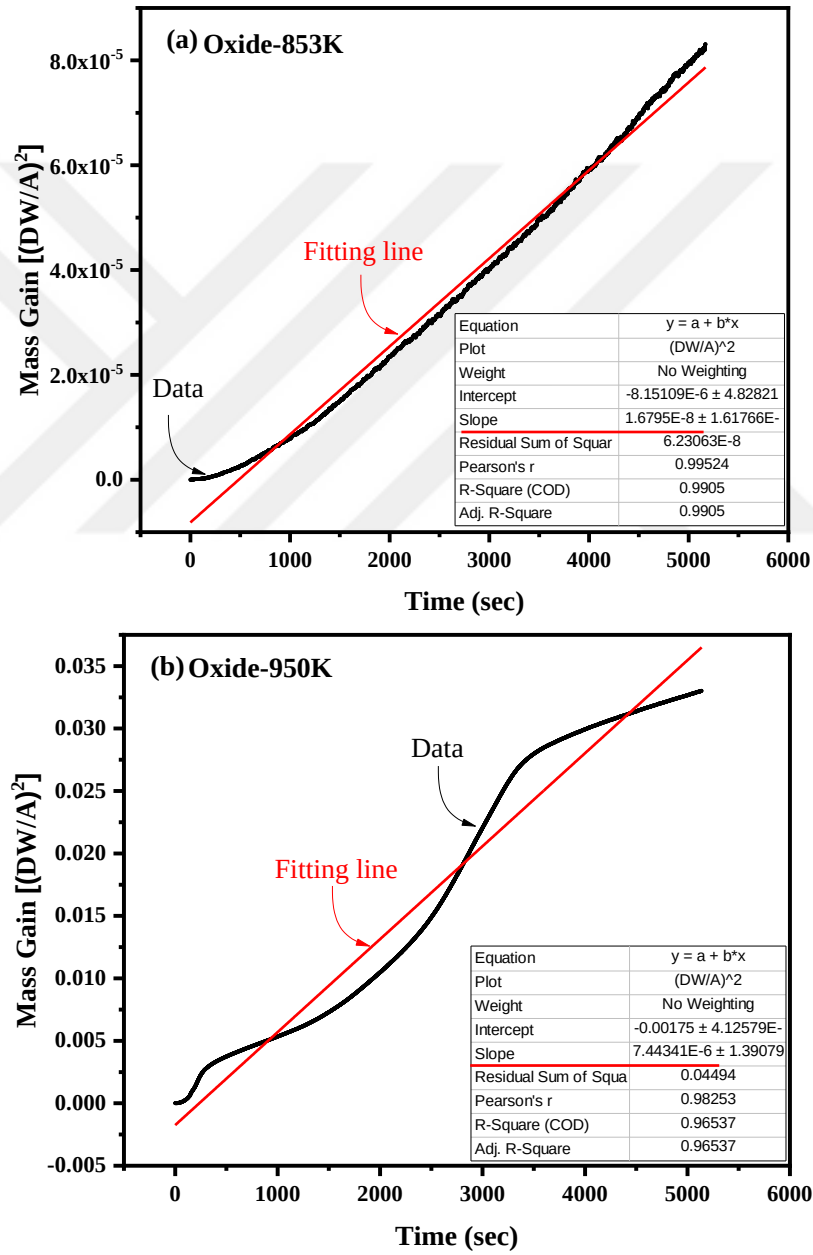


Figure 6.17. The oxidation constant and other correlated parameters for (a) Oxide-853K, (b) Oxide-950K, and (c) Oxide-1225K

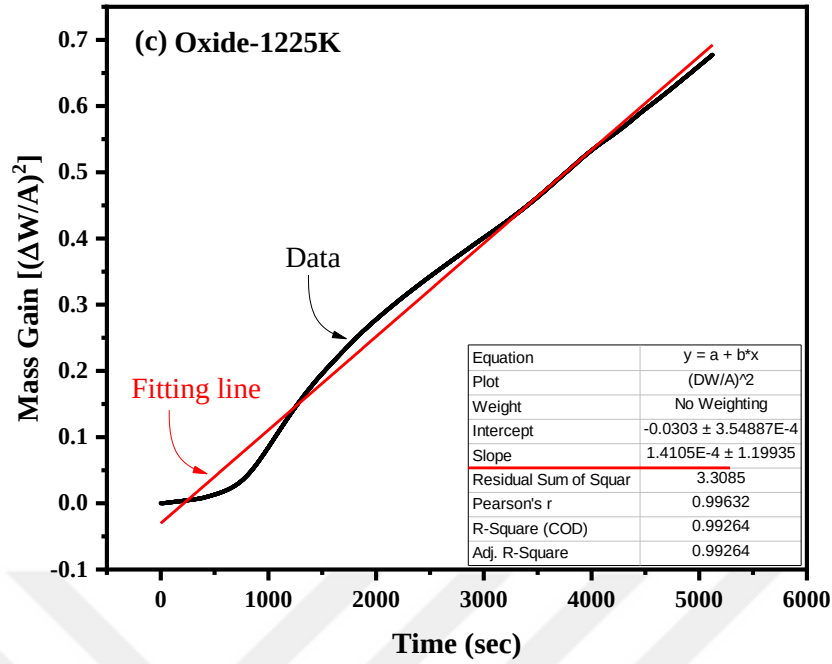


Figure 6.17. The oxidation constant and other correlated parameters for (a) Oxide-853K, (b) Oxide-950K, and (c) Oxide-1225K (continue)

Figure 6.17 illustrates the plotted $(\Delta W/A)^2$ vs. time (sec) and correlated fitting analysis for all oxide samples. The oxidation constant is increased for the isothermal oxidation process carried out at 1225K (Figure 6.18).

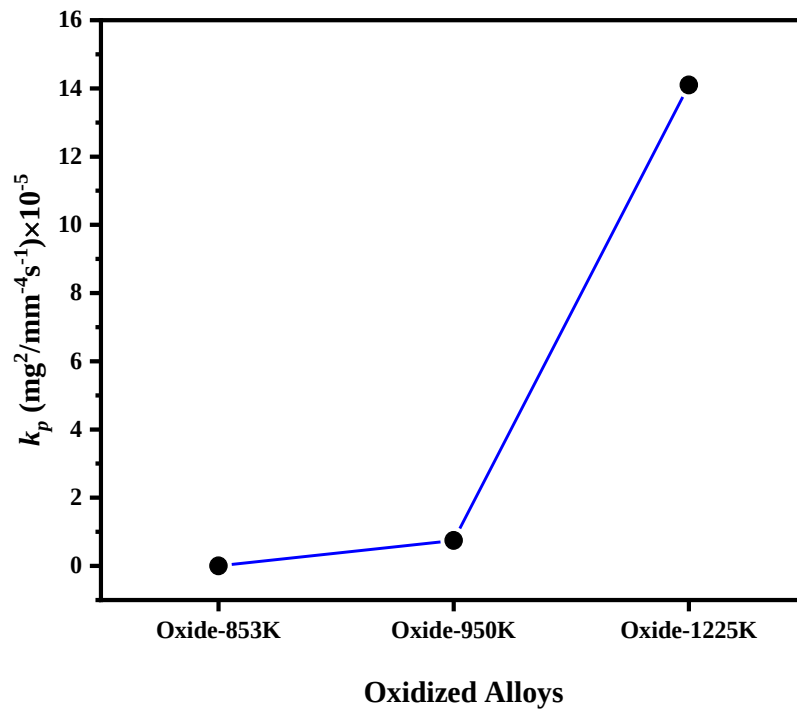


Figure 6.18. The oxidation constant of the NiTiSn alloy

The oxidation process changed some properties of the alloy as well as its appearance. Figure 6.19 displays the samples, which have been oxidized at three different temperatures. The as-cast alloy originally has a light-silver color, which its color changed to gray, yellow, and brown for Oxide-853 K, Oxide-1223 K, and Oxide-1498 K specimens, respectively. The oxidation process in the elevated temperature created a thin film on the alloys, which its thickness and components could affect their color change.

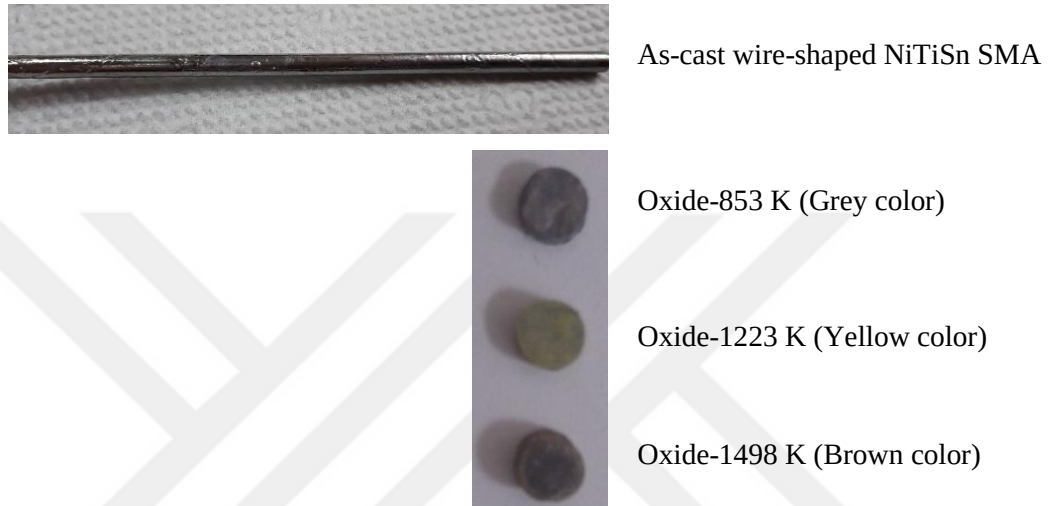


Figure 6.19. The as-cast wire-shaped $\text{Ni}_{47}\text{Ti}_{50}\text{Sn}_3$ (at.%) SMA and the oxidized alloys

The phase transformation temperature was obtained from the onset and endset of the martensitic phase transformations. A tangential line was drawn before starting transformation and another line when the DSC curve approached the peak, then the intercept of these two tangential lines was estimated as the starting of the phase transformation. A similar process was performed to find the endset temperature of the phase transformation. Additionally, the enthalpy change of the phase transformations was found by PerkinElmer software. The aforementioned data is listed in Table 6.6.

Table 6.6. Phase transformation temperatures of the NiTiSn-wire alloys

Samples code	A_s (K)	A_p (K)	A_f (K)	M_s (K)	M_p (K)	M_f (K)	$\Delta H^{M \rightarrow A}$ (J/g)	$\Delta H^{A \rightarrow M}$ (J/g)
As-cast	308.2	324.8	333.5	269	260	243.8	22.5	25.2
Oxide-853K	300.5	315.3	324.2	272.6	263.6	241.6	21	22.6
Oxide-1223K	268.9	293.4	317.5	268	255.8	237.7	21.6	18.3
Oxide-1498K	264.7	276.2	295.3	254.7	244.4	232.3	3.14	0.31

The oxidation process has affected the shape memory characteristics of the alloy because the alloys were subjected to a high temperature for more than one hour. It can be compared to the aging process that is performed in high temperatures. Figure 6.20 shows the DSC results of all oxidized NiTiSn-wire SMAs. It can be seen that $M \rightarrow R$ transformation is disappeared by increasing oxidation temperature. Likewise, Pérez-Sierra et al. testified that aging for a particular time and at a high temperature might have a negative impact on the phase transformation [194]. Therefore, obtaining an oxide film on the surface of a NiTi-based alloy using high temperature has a side effect on the phase transformation, and hence, the alloy can lose its shape memory characteristics. Generally, the martensitic phase transformation diminished by evaluating oxidation temperature.

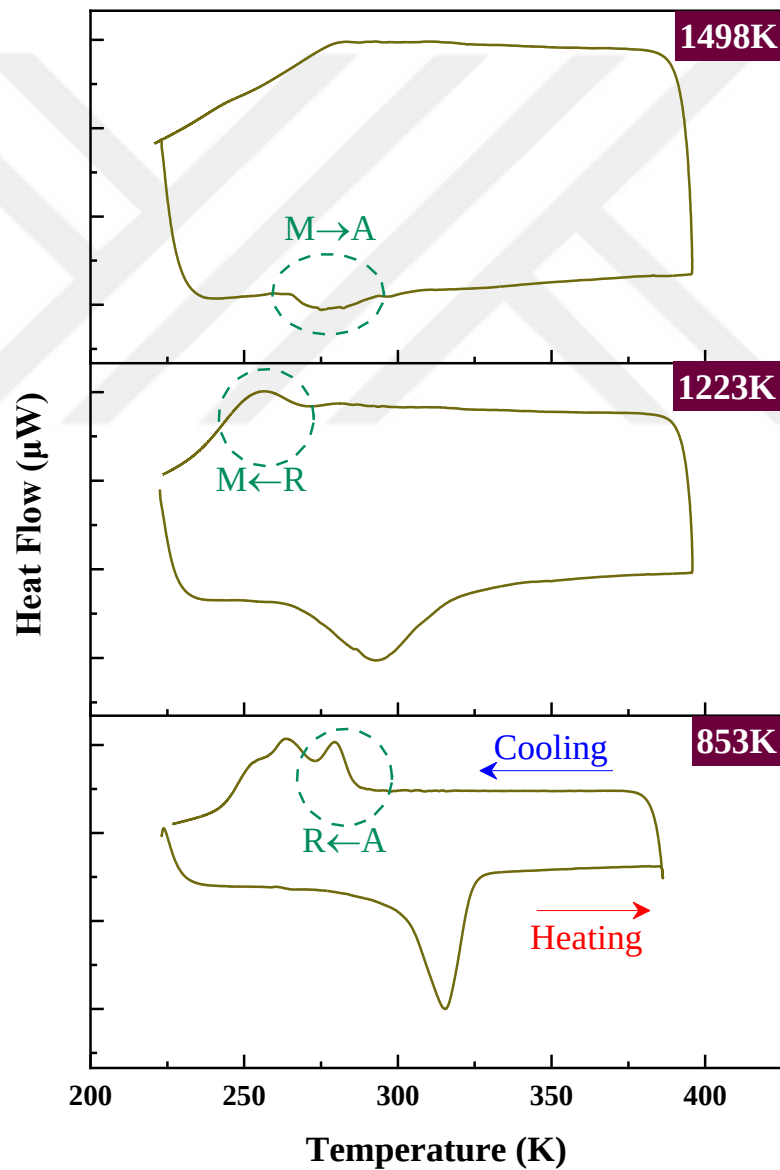


Figure 6.20. The DSC curves of the oxidized NiTiSn alloys in three different isothermal temperatures

Some calculations based on Figure 6.21 and by using equations 6.2a, 6.2b, 6.3, 6.6, and 6.7 were obtained and their values are listed in Table 6.7. The NiTiSn-wire SMA nearly has lost the austenite to martensite phase transformation throughout the cooling process, therefore, the enthalpy and entropy changes of the alloy were affected. The R-phase is also affected by increasing the temperature.

Table 6.7. Some calculated thermodynamics parameters of the NiTiSn-wire alloys

Samples	T_o (K)	$\Delta S^{A \rightarrow M}$ (J/kg K)	$\Delta S^{M \rightarrow A}$ (J/kg K)	$\Delta G^{A \rightarrow M}$ (J)	G_e (J)
As-cast	301	84	75	2409	2108
Oxide-853K	298	75	70	1816	2348
Oxide-1223K	292	63	74	1826	1894
Oxide-1498K	275	1	11	232	25

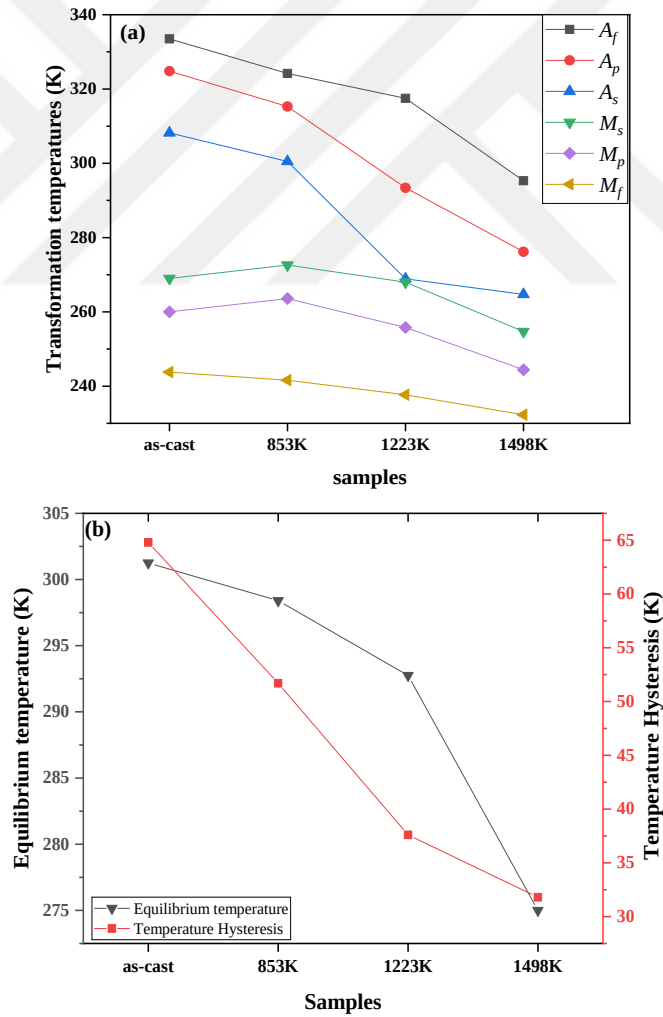


Figure 6.21. (a) Austenite and martensite phase transformations temperatures, (b) Equilibrium temperature, and hysteresis. (c) The enthalpy changes for 5 DSC cycles of the as-cast SMAs. (d) The enthalpy changes for all specimens

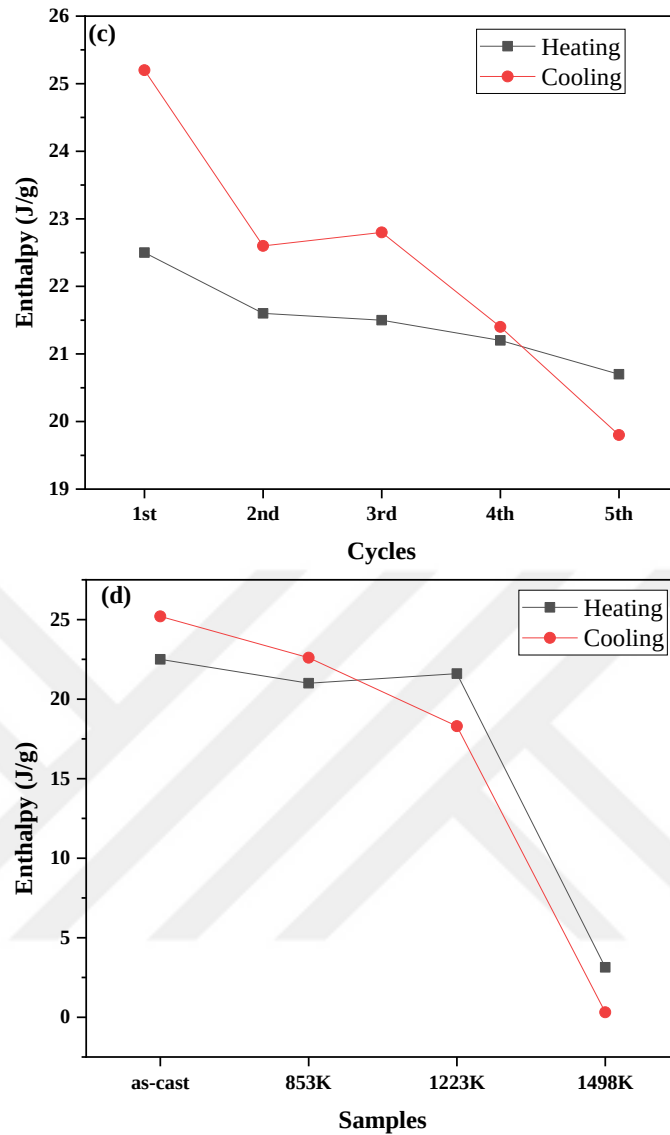


Figure 6.21. (a) Austenite and martensite phase transformations temperatures, (b) Equilibrium temperature, and hysteresis. (c) The enthalpy changes for 5 DSC cycles of the as-cast SMAs. (d) The enthalpy changes for all specimens (continue)

The TTs of the austenite and martensite transformation are listed in Table 6.5. Normally, the energy exchanged during phase transformation can be found by obtaining the area under the heating and cooling DSC-peaks. Based on the DSC results, some thermodynamics properties, including entropy change (ΔS), equilibrium temperature (T_o), Gibbs free energy (ΔG), and elastic energy (G_e) were calculated using the mathematical formula given in Eq. (6.2), Eq. (6.3), Eq. (6.6), and Eq. (6.7), respectively, and the calculated results are listed in Table 6.4. Figure 6.21 demonstrates that the TTs decreased to the lower temperatures, which may generally due to the aging process. A_s in all cases are more than M_s , so it can be concluded that the phase transformations can be classified in Class I [195].

It can be seen that the value of T_0 and temperature hysteresis have dropped down to the lower temperature by applying the oxidation process (Figure 6.21b). Figure 6.21c illustrates the enthalpy change (ΔH) of the heating process, which has diminished through the DSC cycle. On the other hand, the value of ΔH has significantly decreased for the NiTiSn alloy oxidized at 1498 K.

Figure 6.22 demonstrates the XRD pattern of the oxidized NiTiSn-wire SMAs carried out at room temperature. The XRD was indexed by several references and it is found that the oxide alloys contains NiTi (B19') [157], NiTi (B2) [168], TiO_2 [196], Rutile (TiO_2) [191], SnO_2 [197], and Ti_2Ni [198]. Oxide-853K showed the martensite phase (B19') with some oxide phases such as Ti_2Ni and TiO_2 that produced throughout the oxidation process. At room temperature, the XRD measurement of Oxide-1223K showed that the alloy is at the austenite phase. Many oxide phases with different crystal structures and components can be seen in Oxide-1223K. In Oxide-1498K, the Rutile (TiO_2) has covered the surface and there is no nickel element detected in the results.

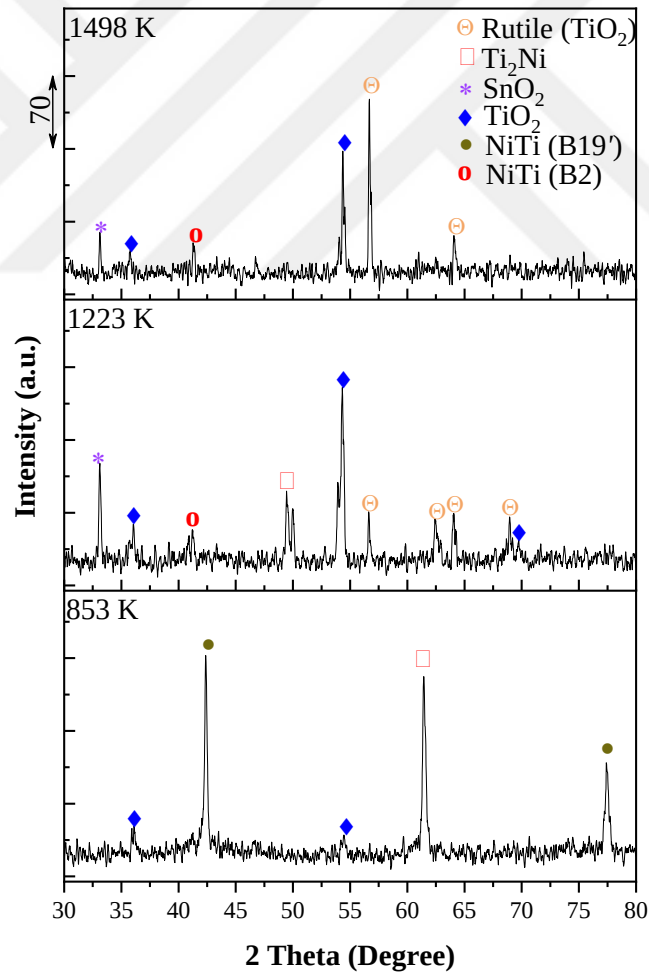


Figure 6.22. The XRD patterns of all the oxidized samples

The nucleation energy (enthalpy change, ΔH_f) for the formation of TiO_2 is $-956 \text{ kJ} \cdot \text{mol}^{-1}$, while the value of ΔH_f for NiO is $-241 \text{ kJ} \cdot \text{mol}^{-1}$ and for SnO_2 is $-570 \text{ kJ} \cdot \text{mol}^{-1}$ [199, 200]. Nickel and tin elements have less affinity to oxygen compared with titanium.

Figure 6.23 reveals the SEM-EDX results of as-cast NiTiSn-wire SMA, Oxide-853K, Oxide-1223K, and Oxide-1498 K. The EDX results of the as-cast NiTiSn alloy is approximately the same as the nominal composition. Table 6.8 lists the compositional ratio based on EDX results. The atomic percentage of the constituents and oxygen elements for the matrix phase is illustrated in Figure 6.23. The total number of Ni atoms has rapidly reduced from the surface by exposing the alloy to the oxidation process. The grains in the oxide-1498K resemble stepped martensite plates, which are well-known as self-accommodating martensite plates [201]. Chu and colleagues [49] stated that oxidation films consist of three layers creates throughout the oxidation process of a NiTi alloy. The layers include rutile (outermost layer), TiO_2 (middle), and $\text{Ni}(\text{Ti})$, TiNi_3 (core).

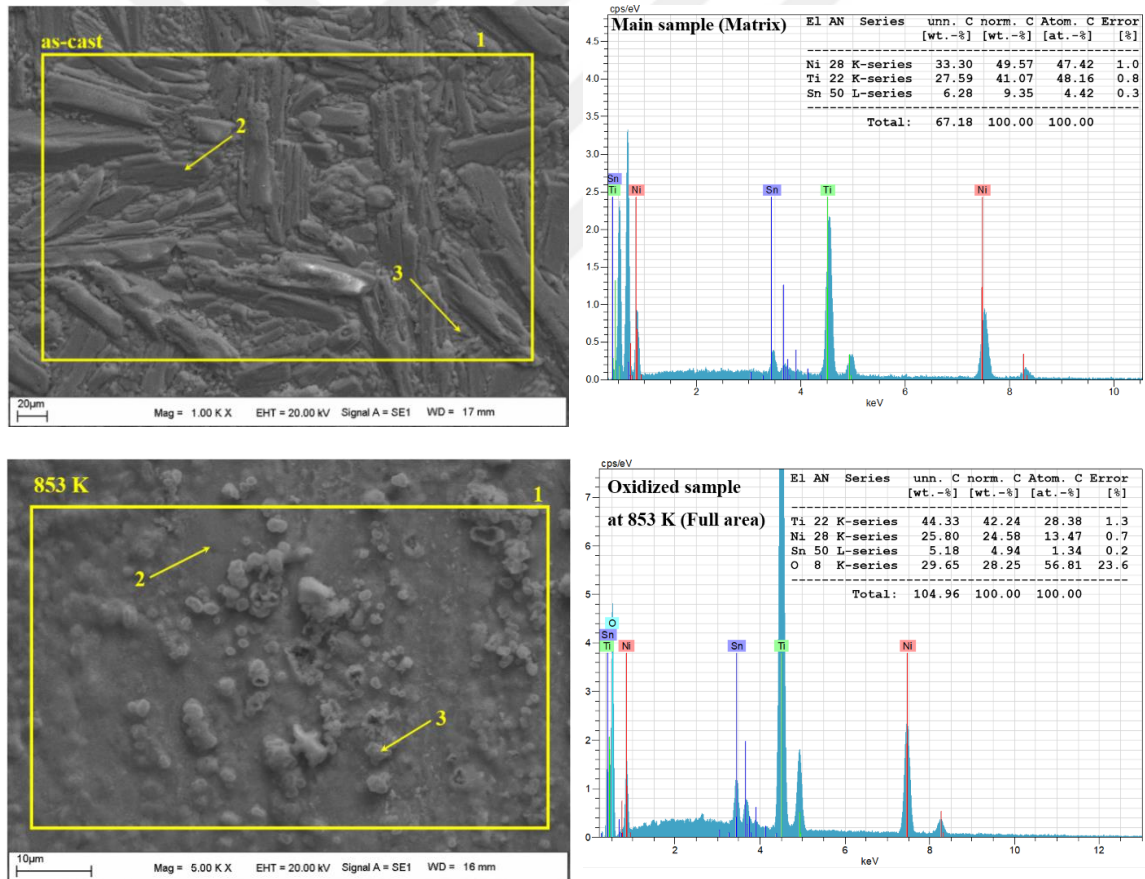


Figure 6.23. The SEM images of the as-cast and oxidized NiTiSn alloys

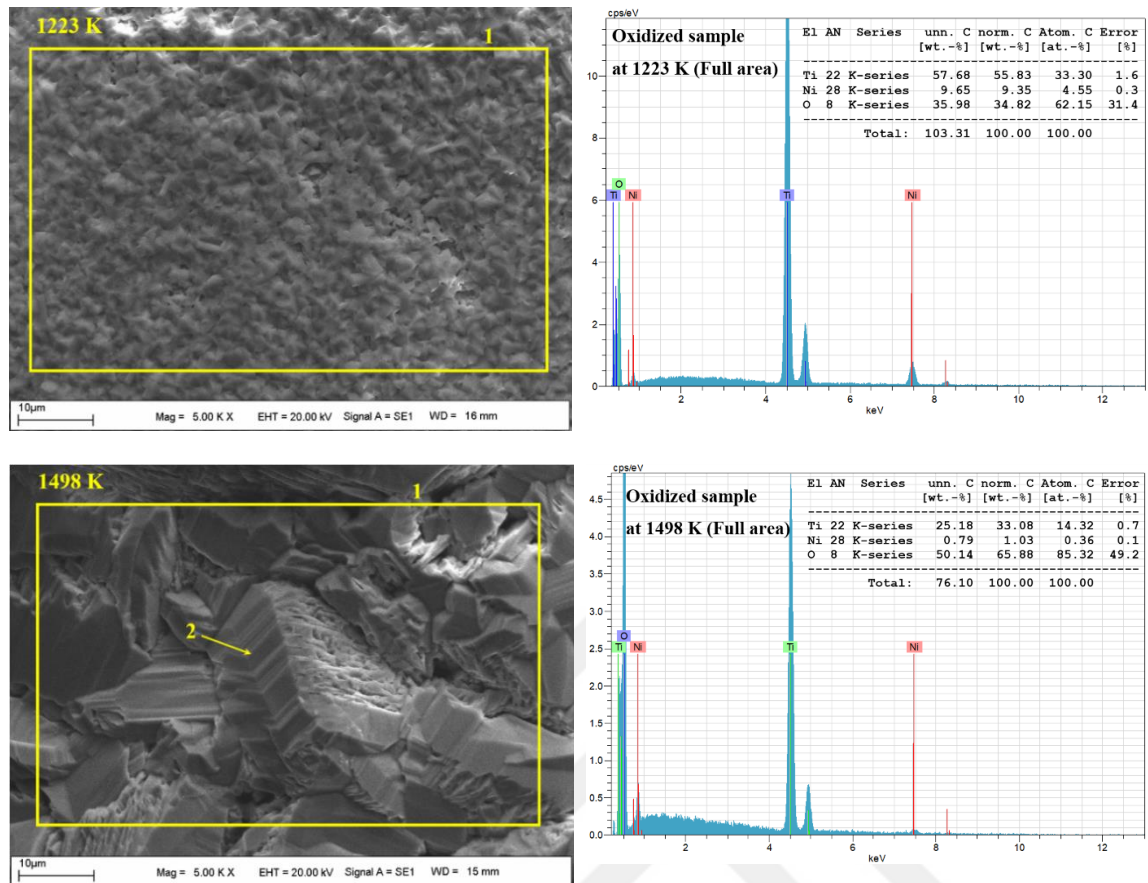


Figure 6.23. The SEM images of the as-cast and oxidized NiTiSn alloys (continue)

Table 6.8. The compositional ratio of different chemical elements obtained from EDS results for the NiTiSn-wire alloys

		Composition (at.%)			
	Spectra	Ni	Ti	Sn	O
As-cast	1 (matrix)	47.42	48.16	4.42	-
	2	48.11	46.36	5.54	-
	3	45.63	51.47	2.89	-
Oxide-853K	1 (matrix)	13.47	28.38	1.34	56.81
	2	25.68	26.52	1.23	46.58
	3	6.73	24.67	0.91	67.70
Oxide-1223K	1 (matrix)	4.55	33.30	-	62.15
Oxide-1498K	1 (matrix)	0.36	14.32	-	85.32
	2	0.09	17.83	-	82.08

Figure 6.24 shows that the amount of oxygen increased on the surface by increasing oxidation temperature. Also, the as-cast NiTiSn-wire SMA, Oxide-853K, Oxide-1223K, and Oxide-1498K were put inside SBF and PS solutions, and after 15 and 30 days, an amount of the solutions were taken for testing with ICP-MS to find the amount of Ni, Ti, and Sn released during those specific periods. The ICP-MS result of the PS solution shows that the amount of Ti and Sn is diminished by increasing oxidation temperature, whereas the proportion of Ni in the Oxide-853K and Oxide-1223K is enhanced compared with the as-cast NiTiSn-wire alloy and Oxide-1498K (Figure 6.25). Additionally, in the SBF solution, Ti is released regularly for all samples, however, the level of Sn is amplified in the Oxide-853K and reduced with rising oxidation temperature. Unlike the other cases, Oxide-1223K has released a lower quantity of Ni into the SBF solution. It is known that Ti and Sn are listed as biocompatible elements [117], so they are passive and do not make a health problem. Besides, it can be seen that the estimated and measured rate of these elements has a good agreement with standards. The expected Ni that may leakage into the SBF and PS solutions is about 60-300 $\mu\text{g/mL}$ for one year, therefore, it can be claimed that the alloys are biocompatible. It is reported that the usual dietary intake of Ni and Ti elements is in the range of 200-300 and 300-2000 $\mu\text{g/day}$, respectively. Furthermore, the dissolved Ni in the normal drinking water is a smaller amount of 20 $\mu\text{g/L}$ and for Ti element is around 0.5-15 $\mu\text{g/L}$ [87, 202-204].

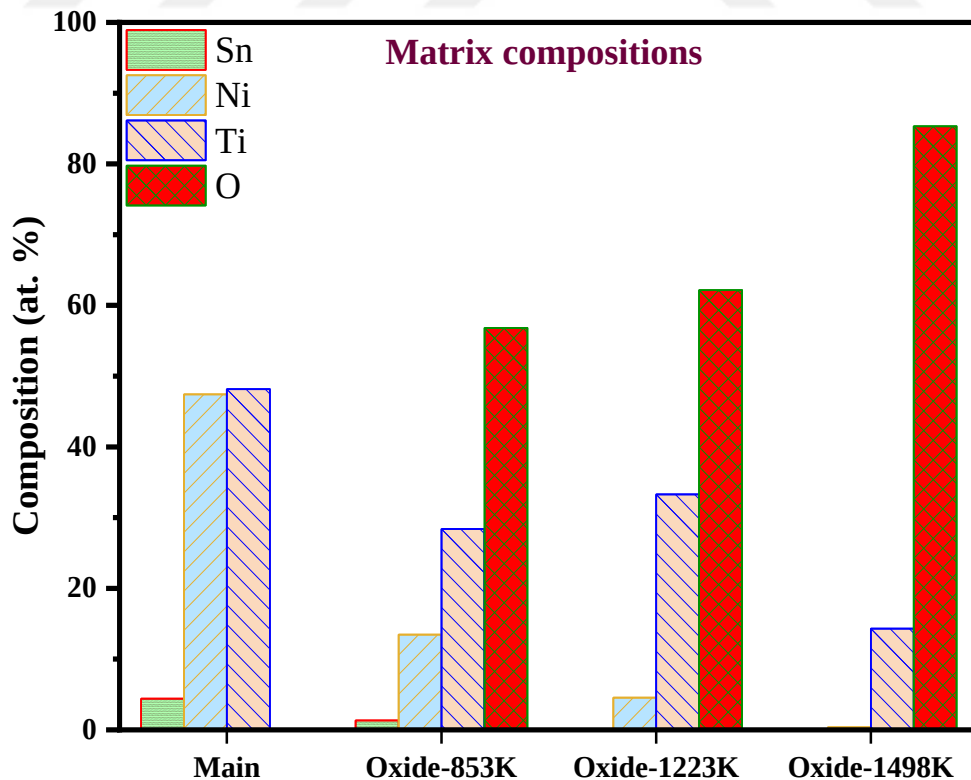


Figure 6.24. Overall EDX results were obtained from samples' matrixes

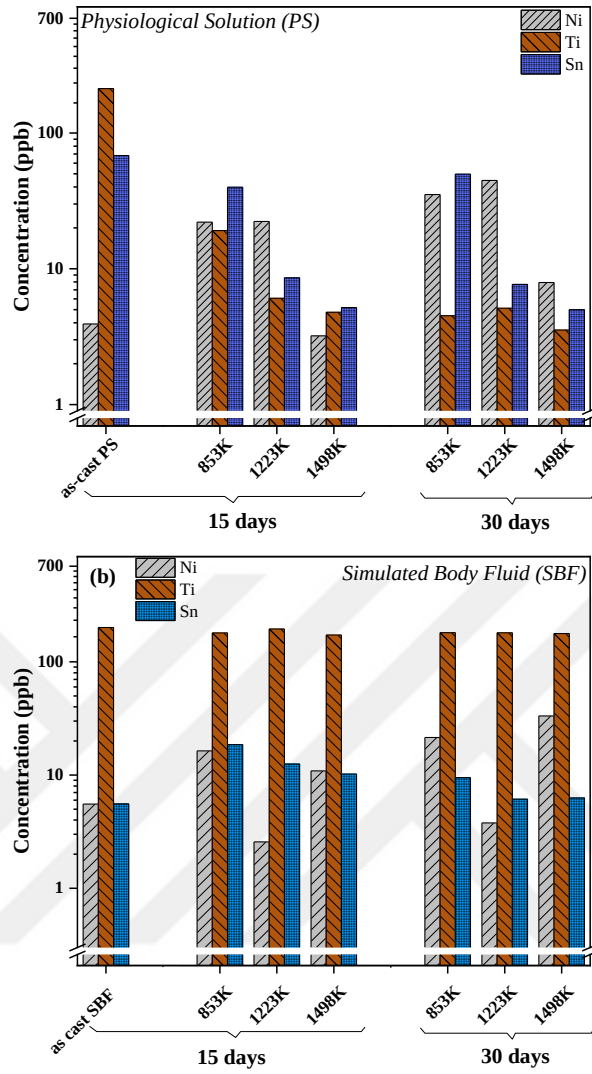


Figure 6.25. The ICP-MS results of (a) physiological solution and (b) simulated body fluid for the as-cast and oxidized NiTiSn wire SMAs

7. CONCLUSIONS

In this study, firstly, different composition of NiTiSn shape memory alloy was prepared by arc melting and they were examined for shape memory behavior and other physical properties. Then one of the compositions was chosen to study its biocompatibility. The first series alloys, including $\text{Ni}_{50-x}\text{Ti}_{50}\text{Sn}_x$ ($x=0.5, 1.0, 1.5, 2.0, 2.5, 3.0$, and 3.5 at. %) showed shape memory, while $\text{Ni}_{50}\text{Ti}_{48}\text{Sn}_2$ and $\text{Ni}_{46}\text{Ti}_{50}\text{Sn}_4$ alloys failed in the as-cast state, even after homogenization. Differential scanning calorimetry, Vickers microhardness, X-ray diffraction, scanning electron microscope, and energy dispersive X-ray spectroscopy were performed on the $\text{Ni}_{50-x}\text{Ti}_{50}\text{Sn}_x$ alloys. Some basic calculations, such as crystallite size and entropy change, were performed using the obtained results and theoretical mathematical models. SEM photos depicted that the alloy was fragmented as the amount of tin (Sn) in the NiTi-based alloy was increased. In the grooves of the fragmentation, there was a sign of Sn elements. Besides, it was discovered that the microhardness and crystallite size of the alloys changed in perfect agreement, showing that the crystallite size influenced the microhardness. By raising the number of cycling processes, the martensite peaks and austenite troughs were shifted to a lower temperature, and the shifting rate was accelerated by replacing more Ni with Sn in the alloy.

Recently, materials with a biocompatible profile have attracted the attention of scientists. The primary goal of this research was to look into the effects of TiO_2 coating and other biocompatible enhancements in the NiTiSn shape memory alloys. To produce a NiTiSn-wire SMA, an expedite composition was chosen. Using an atmosphere-controlled arc-melter, the wire was made from high-purity powders. With temperatures of 853, 1223, and 1498 K, the non-isothermal thermogravimetric profile of the NiTiSn-wire SMA revealed three distinct oxidation behaviors. In normal atmospheric conditions, these determined temperatures were used for a non-isothermal oxidation process for one hour. The oxidation behavior, phase transformation, crystal structure, microstructure, and corrosivity of as-cast and oxidized NiTiSn-wire SMAs were investigated. In addition, the as-cast and oxidized wires were examined in a simulated body fluid (SBF) and physiological solution (PS) at body temperature in an in-vitro test. Since Ti oxidizes more than Sn or Ni, so TiO_2 was the most observed oxide component on the surface of the oxidized alloys. The electrochemical Tafel polarization profile of as-cast NiTiSn SMA revealed that it was more resistant in the physiological serum compared to simulated body fluid at body temperature. In simulated body fluid and physiological serum, respectively, the corrosion rate of the as-cast NiTiSn SMA was 4.81×10^{-4} and 7.86×10^{-4} mm/year, which was discovered to be lower than the value stated for equiatomic NiTi SMAs. The released constituents in both SBF and PS were in high agreement with the standards, according to the compositional assessment of the as-cast and oxidized NiTiSn-wire SMA. For 365 days, the ICP-MS results for Ni were 60-300 $\mu\text{g/mL}$ (for 365 days). Similarly, the amounts of Ti and Sn released met

the requirements. As a result, the NiTiSn-wire SMA has a high likelihood of being implanted in the human body for a variety of purposes.



RECOMMENDATIONS

In this study, Sn with different compositions was alloyed with Nitinol. Also, the main aim was to improve the alloy by coating the surface with TiO_2 . It is recommended to use other techniques like electrical deposition or chemical deposition, instead of oxidation at high temperatures. The aforementioned techniques do not influence the shape memory characterization of the alloy. Also, instead of a ceramic coating layer, it is recommended to use a flexible material that has a good adhesion property and high biocompatibility.



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CURRICULUM VITAE

Ibrahim Nazem QADER

PERSONAL INFORMATION

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RESEARCH EXPERIENCES

- ✓ DSC, TG-DTA, Optical microscope
- ✓ Computer Programming languages available (Python)
- ✓ Computer programs: Microsoft Office Word, Excel, PowerPoint, EndNote, Wolfram Mathematica, Origin Lab, X'pert High Score Plus, Gaussian, ChemBioDraw Ultra, ChemBio3D Ultra, and Inkscape)

WORK EXPERIENCE

2009 – 2011	Assistant Physicist, Salahaddin University-Erbil
2013 – 2014:	Computer Lecturer / Faculty of Education / University of Raparin
2014 – 2016:	General Physics Lecturer / Faculty of basic education - evening / University of Raparin
2014 – 2016:	General Physics Lecturer / Department of Chemistry / Faculty of Science / University of Raparin
2016 – 2017:	Thermodynamics Lecturer / Department of Physics / Faculty of Science / University of Raparin
2015-2016:	Deputy of Physics department / University of Raparin
2015-2016:	Manager of Quality Assurance / Faculty of Science / University of Raparin
2016-2017:	Head of Physics Department / Faculty of Science / University of Raparin

ACADEMIC ACTIVITIES

Paper:

- [1] Qader, I.N., Kok, M., Cirak, Z.D., Pekdemir, M.E., Saydam, S., and Aydogdu, Y. In Vitro Study, Corrosion and Thermal Oxidation Behavior of Wire-Shaped NiTiSn Shape Memory Alloy, *Surface Review and Letters*, Vol. 0 (ja), pp: null. doi: 10.1142/s0218625x21500670.
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Projects:

1. This work was supported by the Management Unit of the Scientific Research Projects of Firat University (FUBAP) (Project Numbers: FF.19.14).
2. This work was supported by the Management Unit of the Scientific Research Projects of Firat University (FUBAP) (Project Numbers: FF.20.06)

