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Propriedades magnéticas das heteroestruturas de NiTi/(Ni, Co)

Diana Lizeth Torres Sánchez

Orientador: Prof. Dr. Daniel Reinaldo Cornejo

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Banca Examinadora:

Prof. Dr. Daniel Reinaldo Cornejo (IF-USP)
Prof. Dr. Adilson Jesus Aparecido de Oliveira (DF-UFSCar)
Prof. Dr. Eduardo Padrón Hernández (DF-UFPE)
Prof. Dra. Márcia Carvalho de Abreu Fantini (IF-USP)
Prof. Dr. Valmir Antônio Chitta (IF-USP)

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Magnetic properties of NiTi/(Ni, Co) heterostructures

Diana Lizeth Torres Sánchez

Supervisor: Prof. Dr. Daniel Reinaldo Cornejo

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Examining Committee:

Prof. Dr. Daniel Reinaldo Cornejo (IF-USP)
Prof. Dr. Adilson Jesus Aparecido de Oliveira (DF-UFSCar)
Prof. Dr. Eduardo Padrón Hernández (DF-UFPE)
Prof. Dra. Márcia Carvalho de Abreu Fantini (IF-USP)
Prof. Dr. Valmir Antônio Chitta (IF-USP)

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To my family.

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Abstract

This thesis focuses on the role of interfacial strain in heterostructures to modify the magnetism of thin ferromagnetic films due to the inverse magnetostrictive effect, defined as the change of magnetization produced in ferromagnetic materials by an external stress. Thus, the magnetic control can be obtained without applying an external field by using heterostructures composed of a non-magnetic layer characterized by a temperature-driven structural phase transition coupled to a ferromagnetic layer. In such heterostructures, the magnetization of the ferromagnetic layer is modified through changes in the stress field at the interface when the structural phase transition in the non-magnetic layer (actuator) is carried out.

In this work, we used NiTi shape memory alloy as the actuator to modify the magnetic behavior of ferromagnetic films through the magneto-elastic coupling in novel NiTi/Ni and NiTi/Co heterostructures. NiTi, when near its equiatomic composition, is a shape memory alloy that undergoes a reversible structural phase transition with temperature, providing stress on the ferromagnetic film. We chose this alloy because NiTi exhibits a large recovery stress with transition temperatures above room temperature for Ti-rich NiTi films, which is of interest for technological applications of the heterostructures.

Since the right microstructure of NiTi is important to observe structural phase transition and it defines the characteristic of the transition, an extensive review on previous research on NiTi is detailed in this thesis. Thus, to ensure large stress during the NiTi structural transition with temperature, the NiTi alloy must be near its equiatomic composition with a thickness above 800 nm. Both characteristics were confirmed by Rutherford Backscattering analyses. The crystal structure and its transition with temperature were studied by X-ray diffraction measurements. In-plane magnetization and hysteresis measurements with temperature, performed on a superconducting quantum interference device (SQUID) magnetometer, prove the magneto-elastic coupling that was observed as an enhancement in the magnetic moment of the ferromagnetic layer. Such enhancement becomes the feature of magneto-elastic coupling in these novel NiTi/ferromagnetic heterostructures.

Key words: Magnetic films, magnetoelastic coupling, inverse magnetostrictive effect, structural phase transition, NiTi shape memory alloy.

Resumo

Esta tese estuda o papel da tensão interfacial em filmes heterogêneos na modificação do magnetismo de camadas ferromagnéticas finas por meio do efeito magnetoestrutivo inverso, definido como a mudança de magnetização produzida em materiais ferromagnéticos por um estresse externo. Tecnicamente, isto visa ter um grau de controle magnético do material sem a aplicação de um campo externo, usando heteroestruturas compostas por uma camada não magnética caracterizada por uma transição de fase estrutural acionada pela temperatura, acoplada a uma camada ferromagnética. Em tais heteroestruturas, a magnetização da camada ferromagnética é modificada através de alterações no campo de tensão na interface quando a transição de fase estrutural na camada não magnética (atuador) é realizada.

Assim, utilizamos a liga com memória de forma NiTi como atuador, para modificar o comportamento magnético de filmes ferromagnéticos através do acoplamento magnetoelástico em novas heteroestruturas de NiTi/Ni e NiTi/Co. O NiTi, quando próximo à sua composição equiatômica, é uma liga com memória de forma que sofre uma transição de fase estrutural reversível com a temperatura, proporcionando tensão no filme ferromagnético. Escolhemos esta liga porque o NiTi apresenta uma grande tensão de recuperação com temperaturas de transição acima da temperatura ambiente, para filmes de NiTi ricos em Ti, o que é de interesse para aplicações tecnológicas das heteroestruturas.

A microestrutura do NiTi é fundamental para favorecer a transição de fase estrutural e definir as suas características. Assim, uma extensa revisão de pesquisas anteriores sobre NiTi é detalhada nesta tese. Para garantir um grande estresse durante a transição estrutural do NiTi com a temperatura, o filme de NiTi deve estar próximo de sua composição equiatômica e ter espessura acima de 800 nm. Ambas as características foram confirmadas pelas análises de espectroscopia de retroespalhamento Rutherford. A estrutura cristalina e sua transição com a temperatura foram estudadas por medidas de difração de raios X. Medidas de magnetização e histerese em função da temperatura, com campo aplicado no plano dos filmes, realizadas em um magnetômetro SQUID, comprovaram a existência do acoplamento magnetoelástico, o qual se manifestou através de

variações no momento magnético da camada ferromagnética. Essas mudanças de magnetização, observadas principalmente na heteroestrutura com Ni, torna-se a característica principal do acoplamento magnetoelástico nesses novos materiais.

Palavras-chave: Filmes magnéticos, acoplamento magnetoelástico, efeito magnetostritivo inverso, transição de fase estrutural, liga NiTi com efeito memória de forma.

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Chapter 1: Introduction

The control of physical properties at the nano-scale is of global interest in the scientific and technological world, in which the constant growth of new technologies associated with small devices has promoted the development of new materials. In magnetism, the control can be obtained for instance in single phase multiferroics as a consequence of the coupling between ferromagnetism with ferroelectricity or the ferroelasticity property. However, the number of single phase multiferroics that naturally exist is limited to a few alloys, and the coupling, although present, is generally weak. Both disadvantages were later overcome by using composites. Thus, heterostructures formed by coupling ferromagnetic films with materials that present a functional property, such as antiferromagnetism, ferroelectric, piezoelectric or multiferroic materials, were successfully used to control magnetism in thin ferromagnetic films. Although in these heterostructures the mechanism of controlling the magnetism is mostly due to an electric field, attention has been recently given to the role of the interfacial strain in magnetic behavior.

In these heterostructures, the interfacial strain modifies the magnetic behavior of ferromagnetic films due to inverse magnetostrictive effect, which is the change of magnetization produced by an external stress. The stress from the actuator, which is the source of the applied stress on the top ferromagnetic layer, can be a result of a reverse piezoelectric response¹, ferroelastic domain switching² or lattice mismatch³, or it can be obtained in materials that undergo structural phase transition with temperature, electric field or any other driven force. Thus, the number of available materials showing magneto-elastic coupling due to interfacial strain is increased by combining different kinds of actuators with ferromagnetic films. The advantages of using each one depend on the applications of the heterostructure. For instance, using piezoelectric materials creates direct and fast control of the magnetic properties by electric fields. However, immediately after

the electric supply is switched off, the strain and the magneto-elastic coupling is usually canceled.

When the actuator displays a structural phase transition with temperature, the transition temperatures and the evolution of the stress on the actuator surface are the features of the structural transition that define the magneto-elastic coupling response in the heterostructures. Among the materials that show structural phase transition, the most well-known is the ferroelectric BaTiO₃ (BTO), which has a perovskite crystal structure. This material has been successfully used as an actuator to obtain magneto-elastic coupling in heterostructures. Ferroelectric BTO has a tetragonal (T) structure below its Curie temperature of 410 K, an orthorhombic (O) structure below 290 K and a rhombohedral (R) structure below 190 K. Previous studies on magneto-elastic coupling in heterostructures formed with BTO had interesting results. Large changes in the magnetization of about 70% and 10% was observed in La_{0.67}Sr_{0.33}MnO₃/BTO at the transition temperatures of BTO⁴. A huge enhancement of in-plane coercivity was also observed in La_{0.7}Sr_{0.3}MnO₃/BTO around the different phase transition temperatures of BTO⁵. Large magnetization changes in Fe/BTO were obtained during the O-R phase transitions of BTO via magneto-elastic coupling⁶. A jump in the magnetization of La_{0.67}Sr_{0.33}MnO₃ was found at the R-O structural transition of BTO in La_{0.67}Sr_{0.33}MnO₃/BTO⁷. The anomaly in the magnetization was attributed to the strain effect in La_{2/3}Ca_{1/3}MnO₃/BTO⁸. In Ga-FeRh/BTO, abrupt changes in magnetization was reported at temperatures of T-O and O-R phase transitions, causing strain induced ferromagnetic-antiferromagnetic phase transition and variations of the magnetic anisotropy in the ferromagnetic phase of FeRh⁹. A giant magnetization variation in FeRh was achieved in FeRh/BTO heterostructures mostly driven by voltage-induced strain from BTO¹⁰. In FeRh/BTO, the compressive strain at T-O and O-R stabilized the antiferromagnetic state of FeRh and induced large drops of magnetic moment¹¹. In the studies mentioned above, one limitation of BTO could be the temperature at which the T-O and R-O phase transformation occurs, which is below room temperature.

Actuators other than BTO were found in Graczyk et al.¹², who saw a significant change in NiFe film magnetization in NiFe/LiCsSO₄ and NiFe/KH₂PO₄ as a consequence of magneto-elastic coupling through the structural phase transition of the substrates. De la Venta et al.¹³ obtained a

reversible change in the magnetic coercivity of V_2O_3/Ni bilayers, attributed to interfacial stress originating from the structural phase transition observed in vanadium oxide. These examples of heterostructures enable a new means of modifying the magnetic properties of ferromagnetic films without applying an external field by using actuators that exhibit structural phase transition with temperature.

In this thesis, we propose another actuator as the source of interfacial strain. To choose the actuator, we searched for materials showing structural phase transition with temperature. In particular, we looked for martensitic phase transformation because it does not require large displacement of atoms, ensuring the reversibility of the transition. We were also interested in transformation temperatures close and above room temperature in order to use the heterostructures in future applications. Also, we search for actuators that exhibit large change of mechanical stress on its surface during the transition. By considering these three conditions, we propose NiTi alloy as the actuator. NiTi is a well-known shape memory alloy showing structural phase transition with temperature and with transition temperatures between 50 and 100 °C for Ti-rich NiTi films. NiTi alloys exhibit the shape memory effect, which is the ability to remember its geometry by heating after being deformed. This effect is associated with the reverse martensitic transformation, which changes from a monoclinic phase at low temperatures to the austenite phase at higher temperatures. NiTi alloys show also a great variation in the stress on their surfaces during the structural transition which is important to obtain a high effect on the ferromagnetic layer (Ni, Co) via the magneto-elastic coupling. Therefore, the aim of this thesis is to study the magnetic behavior of NiTi/(Ni, Co) heterostructures through the structural phase transition of NiTi.

The following chapters will be divided as follows. Chapter 2 describes the fundamental concepts needed to understand the magneto-elastic coupling in NiTi/ferromagnetic heterostructures and the properties of NiTi shape memory alloy, focusing on the structural phase transition. In Chapter 3, we explain the experimental techniques employed for the preparation and characterization of the heterostructures, providing an overview of sputtering conditions of NiTi films to obtain the shape memory effect in attached films. Chapter 4 illustrates the chemical analyses obtained by Rutherford Back Scattering spectrometry (RBS) to determine that NiTi alloys were near

equiatomic composition and with thicknesses above 800 nm to ensure large strains during the transition. This chapter also discusses the crystalline structure of NiTi films and NiTi/(Ni, Co) heterostructures deposited on Si(100), which were studied by X-ray diffraction (XRD) measurements. Chapter 5 provides the magnetic studies by in-plane magnetization and magnetic hysteresis loops with temperatures through the structural phase transition of NiTi. Also, the magneto-elastic effect in the heterostructures is explained. Finally, in Chapter 6, we provide the conclusions of our results.

Chapter 2: Fundamental concepts

To understand magneto-elastic coupling in the NiTi/(Ni, Co) heterostructures, the magnetic properties of ferromagnetic films, followed by the description of the inverse magnetostrictive effect, is discussed in this chapter. Then, the properties and shape memory effect of NiTi are detailed to outline the features of the interfacial strain that causes the magneto-elastic coupling in the heterostructures.

2.1. Magnetic properties of ferromagnetic films

2.1.1. Energy terms

Ferromagnetic materials are characterized by their spontaneous magnetization (i.e., magnetization even in the absence of an applied field) below a critical temperature T_c , called Curie temperature. This long-range magnetic order was not understood until 1907 when Weiss¹⁴ introduced the concept of the molecular field to explain the ordering. The molecular field is a strong field inside all ferromagnetic materials that aligns adjacent spins within regions, called domains, which are magnetized to the saturation state M_s . In a demagnetized state, the atomic magnetic moments are randomly aligned from one domain to the next.

In a ferromagnetic sample, the magnetization depends on the total energy, E , in the system, which is the result of the following energies:¹⁵

- Potential or Zeeman energy, E_z : energy of the domains or total magnetic moment in the presence of an applied field $\vec{H}$. $E_z = - \int_V \mu_0 \vec{M} \cdot \vec{H} dV$.

- Exchange energy, E_{ex} : energy associated with the exchange interaction between neighboring magnetic moments. $E_{ex} = -\sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$, where i and j are the sites of spins $\vec{S}_i$ and $\vec{S}_j$, and $J_{ij} > 0$ for the nearest neighbors in ferromagnetic samples.
- Magnetostatic energy, E_{ms} : Also called dipolar energy, the magnetic energy of the magnetization in the demagnetizing field, $\vec{H}_d$, which is the magnetic field that the sample itself creates. $E_{ms} = -\frac{1}{2} \mu_0 \int_V \vec{H}_d \cdot \vec{M} dV$; $\vec{H}_d = N_d \vec{M}$, where N_d is the demagnetizing factor and, for the plane shape, $N_d = 1$ or 0 for perpendicular or parallel directions, respectively.
- Magnetic anisotropy energy, E_A : occurs when the magnetization has a preference for a particular direction. Magnetic anisotropy energy can be obtained due to crystal symmetry, stress, sample shape or other sources of anisotropy. The energy associated with anisotropy of crystallites gives the magnetocrystalline energy, E_{mc} . The energy associated with the stress through the inverse magnetostrictive effect gives the magneto-elastic energy, E_{me} .

Thus, the total energy is as follow:

$$E = E_z + E_{ex} + E_{ms} + E_A \quad (2.1)$$

$$E_A = E_{mc} + E_{me} + others \quad (2.2)$$

In reduced dimensions as it is in ferromagnetic thin films, the magnetization is usually parallel to the plane to reduce the magnetostatic energy. Thus, ferromagnetic films mostly show in-plane anisotropy due to their strong shape anisotropy, a constant term involved in the magnetostatic energy. In ferromagnetic domains with in-plane anisotropy, magnetic domains form stripes separated by Néel walls (Fig. 2.1) for thicknesses below 50 nm¹⁶. In polycrystalline materials, the domain structures are essentially determined by the size of the grains¹⁴. The critical size D_{cr} , or the largest size of a ferromagnetic particle still considered a monodomain, varies from about 10 nm to thousands of nanometers (or microns) depending on the material. For Ni and Co ferromagnetic metal, this critical diameter is 50 nm and 100 nm, respectively¹⁷.

Fig. 2.1. Rotation of the magnetization in a Néel wall¹⁸.

In a polycrystalline ferromagnetic sample, the crystallites (grains) are randomly oriented, and because each crystallite has an easy axis of magnetization, the sample has random directions of easy magnetization. Polycrystalline samples without a preferred orientation of grains do not possess any magnetocrystalline anisotropy¹⁸. Therefore, if the ferromagnetic layer in an actuator/ferromagnetic heterostructure is polycrystalline then only the magneto-elastic energy modifies the anisotropy energy in the ferromagnetic layer, considering the absence of other anisotropies.

2.1.2. Magnetization of ferromagnetic films

The process of magnetization of a ferromagnetic material involves converting the specimen from a multi-domain state to a single domain state magnetized in the same direction as the applied field. This process is illustrated in the magnetization curve in Fig. 2.2. By increasing the applied field on a sample from a demagnetized state, the domain walls start to move and some domains begin increasing in size. At this stage, the process is still reversible because if the field is removed, the material can return to its previous state without hysteresis. In the next stage, there is a fast increase in the magnetization where the domain walls move irreversibly (i.e., the sample will remain partly magnetized if the field is removed). By further increasing in the magnetic field above the knee point, the single domain starts to rotate, and the magnetization increases by rotation until it gets aligned with the magnetic field, the state near saturation. Polycrystalline materials have randomly distributed grains; therefore, the magnetization curve will be an average of the magnetization of these grains.

Fig. 2.2. Typical initial magnetization curve for ferromagnetic materials¹⁵.

In a ferromagnetic material, the magnetization reversal forms a hysteresis loop. The magnetization decreases, creating a different path than that of the forward magnetization process, when the magnetic field decreases from the saturated state. This is a consequence of the irreversible processes during the magnetization of the sample under an applied field, as explained in the previous paragraph. A typical shape of a hysteresis loop of a ferromagnetic sample is illustrated in Fig. 2.3. The following two parameters are the most important in magnetic hysteresis loops: the remanent magnetization or remanence, M_r , and the coercivity, H_c . M_r is the magnetization at the zero field of a sample coming from a saturated state. This parameter represents the fact that a ferromagnetic sample can be spontaneously magnetized even in the absence of an external field¹⁹. The coercivity, or coercive field H_c , is the field needed to bring the magnetization from the remanent value to zero. This parameter measures the order of magnitude of the field that must be applied to a material to reverse its magnetization; therefore, this value is used to classify the difficulty of a material to become magnetized. For a polycrystalline alloy, the random orientation of the magnetization between the domains means that the induced anisotropy directions in the various domains will also have a random orientation. This results in a constricted hysteresis loop²⁰.

Fig. 2.3. Magnetic hysteresis loop: Magnetization, M , vs magnetic field, H . M_r is the magnetic remanence. H_c is the coercive field, and the virgin curve represents the response of the magnetic moments on the first sweep of the field¹⁶.

Spontaneous magnetization, a characteristic of ferromagnetic materials, vanishes at temperatures above Curie temperature, T_c (Fig. 2.4(a)). Thus, T_c represents the highest temperature at which the ferromagnetic order can be found. For Ni and Co, the Curie temperature is 631 K and 1394 K, respectively²¹. The analysis of magnetization as a function of temperature can be achieved by recording Zero Field Cooled (ZFC) and Field Cooled (FC) curves. The ZFC curve is recorded after the sample is firstly cooled without applying any magnetic field, to reach the temperature at which the measurement begins. At this point, a particular magnetic field is applied, and the magnetization is measured during heating. The FC curve is recorded during cooling in the presence of the applied field. A typical response, the ZFC and FC curves, of a ferromagnetic material is depicted in Fig. 2.4(b).

Fig. 2.4. (a) Magnetization as a function of temperature for ferromagnetic materials (modified from Blundell). (b) Temperature dependence of the field-cooled (FC) and zero field-cooled (ZFC) moments.

2.1.3. Superparamagnetism

In small ferromagnetic particles, surface energy, such as domain wall energy, becomes much costlier than volume energy, such as demagnetizing energy. To minimize the energy, the particles avoid the formation of magnetic walls and become single domains. The magnetization of these particles always lies parallel or antiparallel to a particular direction with anisotropy energy density ($E = K_{eff}V \sin^2 \theta$, where K_{eff} is the effective anisotropy density constant, V is the particle volume and θ is the angle between the magnetization and the easy direction). The minimum energy is obtained at 0° and 180° , and the activation energy to flip the magnetization of the particle is $K_{eff}V$. For small particles, $K_{eff}V$ is smaller than thermal energy $k_B T$, and the magnetization can easily be flipped by thermal fluctuations. In a distribution of these small particles (when $k_B T \gg K_{eff}V$), the system will behave paramagnetically if the particles are in a non-magnetic medium and without interaction between particles. Therefore, the moment in each particle will be the sum of all atomic moments inside the particle. This system is called a superparamagnetic system, and at high temperatures, the moment of each particle fluctuates rapidly. The relaxation time is given by the following equation²¹:

$$\tau = \tau_0 \exp\left(\frac{K_{eff}V}{k_B T}\right) \quad (2.3)$$

The system appears static when the relaxation time is much longer than the measuring time, t , consider as $\tau > \alpha t, \alpha = 100$. τ_0 is usually 10^{-9} s. Then, the particle is locked in one of the two minima energies below the blocking temperature defined by the following equation:

$$T_B = \frac{K_{eff}V}{k_B \ln(\alpha t / \tau_0)} = \frac{K_{eff}V}{25 k_B}, \quad (2.4)$$

During heating, initially, the thermal energy $k_B T$ is much smaller than the anisotropy barrier $K_{eff}V$, so the magnetization remains null. Due to the exponential dependence of the relaxation time on temperature when $k_B T \sim K_{eff}V$, the magnetization grows rapidly to its thermodynamic equilibrium value. The blocking temperature is considered the inflection point of this growth. In

ideal systems, for a monosize non-interacting magnetic nanoparticles sample, the blocking temperature is well defined. Real samples always present size dispersion, which is usually reasonably well described by a log-normal distribution. A different particle size implies a different anisotropy barrier ($K_{eff}V$) and therefore a different T_B for each size fraction, so in real ZFC-FC experiments, the blocking region is wide and a representative T_B value of the ensemble is not well-defined.

2.2. Inverse magnetostrictive effect

The change in the length of a ferromagnetic material under an applied field was first observed by Joule in 1842 on an iron rod. This phenomenon is called Joule magnetostriction, or simply the magnetostrictive effect, and is a consequence of the reorientation of the magnetic domains when subjected to a magnetic field. The fractional change in length ($\Delta l/l$) is a strain and is called magnetostriction, λ . In a crystal, this quantity depends on the direction relative to the crystal axes at which magnetostriction is analyzed, the direction of saturation, and the individual magnetostriction in the direction of the crystal axes. For instance, in a cubic crystal that changes from a demagnetized state to the saturation in a direction defined by α_1 , α_2 , and α_3 , the saturation magnetostriction (λ_{si}) measured in a direction defined by the cosines β_1 , β_2 , and β_3 relative to the crystal axes is given by the following equation:²²

$$\lambda_{si} = \frac{3}{2} \lambda_{100} \left(\alpha_1^2 \beta_1^2 + \alpha_2^2 \beta_2^2 + \alpha_3^2 \beta_3^2 - \frac{1}{3} \right) + 3\lambda_{111} (\alpha_1 \alpha_2 \beta_1 \beta_2 + \alpha_2 \alpha_3 \beta_2 \beta_3 + \alpha_3 \alpha_1 \beta_3 \beta_1), \quad (2.5)$$

where λ_{100} and λ_{111} are the saturation magnetostriction when the crystal is magnetized, and the strain is measured in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, respectively.

In polycrystalline materials, the situation is more complex than in single crystals because one has to relate the magnetostriction of the whole piece of material to the magnetostrictive properties of the individual grains. Also, the strain response of the grain to the magnetic field will be influenced by neighboring grains since grains are randomly oriented in polycrystals. Therefore, the saturation magnetostriction of the polycrystal cannot be solved by a simple averaging procedure. However, if it is assumed that the material is composed of a large number of domains

with a uniform strain in all directions then for an untextured polycrystal and for amorphous alloys, the magnetostriction can be expressed as follows²⁰: $\lambda_s = \frac{2}{5} \lambda_{100} + \frac{3}{5} \lambda_{111}$. Thus, the obtained value of λ_s for Ni polycrystalline is -34×10^{-6} .

The inverse effect to Joule magnetostriction is also observed on ferromagnetic materials. By stressing or straining a magnetic material, a change in its preferred magnetization direction is produced, which is manifested in its magnetization curve (Fig. 2.5). In this case, the effect is called the inverse magnetostrictive effect, also known as the Villari effect, which is the change in magnetization produced by an external stress²³.

Fig. 2.5. Effect of an external stress on the magnetization²⁴.

The magneto-elastic energy associated with the stress or induced stress anisotropy (E_{me}) is given by the following equation²²:

$$E_{me} = \frac{3}{2} \lambda_{si} \sigma \sin^2 \theta, \quad (2.6)$$

where λ_{si} is the saturation magnetostriction, and θ is the angle between the saturation magnetization, M_s , and the external stress, σ . In this equation, the axis of stress is an axis of easy magnetization if $\lambda_{si} \sigma > 0$. In the opposite case, where $\lambda_{si} \sigma < 0$, the axis of stress is a hard axis and the plane normal to the stress is an easy axis.

In Eq. 2.6, $K_\sigma = \frac{3}{2}\lambda_{si}\sigma$ is called the stress anisotropy constant. By assuming uniform stress, the coercivity caused by the stress anisotropy field is given by the following equation²²:

$$H_{K_\sigma} = \frac{2K_\sigma}{M_s} = \frac{3\lambda_{si}\sigma}{M_s}, \quad (2.7)$$

where σ is the stress in MPa, and M_s is the saturation magnetization in G or emu/cm³.

2.3. NiTi shape memory alloys

NiTi, also known as nitinol, is a shape memory alloy discovered in the 1950s. Shape memory alloys are metals that after being deformed can remember their geometries by unloading at a higher ambient temperature (superelasticity) or by heating (shape memory effect, SME)²⁵. The latter has a great importance in micro-electro-mechanical systems in which equiatomic NiTi alloys are the most promising due to their interesting properties, such as large stress and large displacement with change in temperature, large recovery force, low operating voltage, good chemical resistance and biocompatibility²⁵.

The SME in equiatomic NiTi is associated with the thermoelastic martensitic phase transformation from which the large stress is obtained. Martensite transformations are diffusionless, ensuring the reversibility of the transformation. In NiTi, this transformation is given between two defined crystal structures due to change in temperature. The NiTi transformation goes from a cubic austenite B2 phase at high temperatures to a monoclinic martensite B19' phase at lower temperatures. The inverse transformation during heating is called the reverse martensitic phase transformation²⁶⁻²⁸. The phase transition temperatures occur above room temperature and between 50 and 100 °C for Ti-rich NiTi films^{29,30}, which is ideal for future applications. The crystal structure of martensite and austenite phases of NiTi are depicted in Fig. 2.6. Lattice parameters obtained by single crystal XRD for B19' of Ti-49.2 at%Ni alloy are as follows: $a = 0.2898$ nm, $b = 0.4108$ nm, $c = 0.4646$ nm and $\gamma = 97.78^\circ$ ³¹; while B2 phase at room temperature has a lattice constant of 0.3015 nm³².

Fig. 2.6. Crystal structure of NiTi alloy. Left: Austenite cubic B2 cell (shadow box). Right: Monoclinic B19' phase. Ni and Ti atoms are represented by red and blue balls, respectively³³.

The reverse martensitic and martensitic transformations in NiTi produce a thermal hysteresis of the stress on its surface as illustrated in Fig. 2.7. Such hysteresis is defined by the transition temperatures (austenite transition start temperature (A_s), austenite transition finish temperature (A_f), R-phase transition start temperature (R_s), R-phase transition finish temperature (R_f), martensite transition start temperature (M_s) and martensite transition finish temperature (M_f)); the residual stress, which is the remaining stress at room temperature; and the recovery stress, which is given by the difference between the stress at A_f and the stress at M_f . In the transition, the R-phase is an intermediate phase that NiTi can exhibit during cooling.

Fig. 2.7. Typical thermal hysteresis of stress versus temperature of $\text{Ni}_{0.5}\text{Ti}_{0.5}$ film on Si^{25} . The austenite transition start temperature is depicted by A_s , the austenite transition finish temperature by A_f , the R-phase transition start temperature by R_s , the R-phase transition finish temperature by R_f , the martensite transition start temperature by M_s , and the martensite transition finish temperature by M_f .

The performance of the SME in NiTi is influenced by parameters associated with the microstructure characteristics of the films (chemical composition, annealing process and grain size) and the thickness of NiTi. Also, to use NiTi films as actuators, we want to obtain large recovery stress and minimum residual stress in attached NiTi films. To achieve this, according to Fu et al.³⁴, these requirements are needed: (1) precisely control Ti/Ni ratio; (2) deposit films at a possible lower pressure; (3) select a suitable deposition temperature or annealing temperature, compromising between thermal stress and intrinsic stress; (4) use some interlayers (with possible compressive stress) to reduce large tensile stress in some NiTi films.

The influence of chemical composition on the performance of the SME is depicted in Fig. 2.8, which illustrates the stress of attached NiTi films as a function of temperature from two independent studies. In both studies, films were prepared under the same sputtering conditions but at different argon gas pressures. Films in Fig. 2.8(a) were deposited at 1 mTorr and in Fig. 2.8(b) at 3.2 mTorr. In both studies, although the chemical composition was similar between the

NiTi films, the films displayed different characteristics in their structural phase transition deduced from the difference between the hysteresis shapes. The research also found that the residual stress decreased as the atomic percentage of Ti increased. Furthermore, the highest recovery stress was obtained for films with 50.4% and 50.2% of Ti, resulting in an increase in the austenite transition start temperature. The difference in argon gas pressure did not affect the general relationship between recovery stress and Ti content.

Fig. 2.8. Stress evolution of NiTi films with different Ti/Ni ratios. a) Films were deposited at 450 °C with 1 mTorr of argon gas pressure^{25 34}. b) Films were deposited with 3.2 m Torr of argon gas pressure on Si substrate using 200 nm of SiN as an interlayer between the film and the substrate²⁹.

The residual stress also decreased as the content of Ti gradually increased to 51.3%, as illustrated in Fig. 2.9. However, for further values of Ti content, the opposite behavior was observed. Additionally, an annealing process reduced the residual stress in films with Ti content up to 51.3%.

Fig. 2.9. (a) Residual stress for NiTi films with different Ti/Ni ratios at an Ar gas pressure of 3.2 mTorr³⁴. (b) Stress measurements results for NiTi films with different Ti contents and post-annealing temperatures. Ar gas pressure of 2.3 mTorr³⁵.

The difference in the residual stress of films deposited at different argon gas pressures is displayed in Fig. 2.10. Since films were deposited at room temperature, thermal stress was

considered insignificant. Then, the residual stress at different argon gas pressures was attributed to the intrinsic stress during film nucleation and growth. Films deposited at 0.8 mTorr indicated a compressive stress, which is often suitable for technological applications because films are stronger in compressive than in tension stress.

Fig. 2.10. Changes of residual stress for the as-deposited films under different Ar gas pressures as a function of film thickness³⁴.

Attached NiTi films are under a strong interaction at the interface that could suppress the SME, whereas NiTi peeled off from the substrate has a free martensitic transformation. Therefore, phase transition temperatures could be significantly different between NiTi films peeled off and films attached to the substrate, depending on their crystalline phase at room temperature. If most of the crystalline structure is in the martensite phase, the transformation temperatures are similar. Otherwise, transformation temperatures are significantly different since the martensite phase has weak interaction with the substrate. Kabla et al.³⁶ concluded that the inhibition of martensitic transformation in films, which show austenite and R-phase at room temperature, is a result of the combination of small grains and strain constraints caused by the substrate. The authors reported that NiTi films with grains larger than 150 nm undergo a martensitic phase transformation at a temperature of 50 °C, while neighboring grains smaller than 50 nm^{36,37} do not transform into martensite, even after being cooled with liquid nitrogen. However, obtaining large grains with a controlling process is difficult because the grain growth process tends to increase the grain size, but then a faster nucleation rate tends to decrease it.

Another important parameter to observe the shape memory effect is the thickness of the films. Researchers observed that the effect only appears in films with thicknesses higher than 200 nm, as depicted in Fig. 2.11. Less than this value, the effect is barely observed because the oxide layer formed on the top of the film, and the inter-diffusion layer between the film and the substrate become dominant, restricting the phase transformation^{27,38,39}. Researchers also observed that the recovery stress significantly increases as the film thickness increases, reaching a maximum value for film thickness of 820 nm. Then, recovery stress decreases gradually for larger values in thickness. This finding is in agreement with the highest strain transformation observed for thickness around 1 to 2 μm ³⁸. The constraints from neighboring grains increase as the thickness increases, whereas the constraints from the surface oxide layer increase when the thickness decreases³⁸.

Fig. 2.11. Stress-temperature evolution curves for NiTi films with different thickness²⁷.

Finally, precipitates formed during the production of NiTi alloys influence the shape memory effect. As the phase diagram of NiTi system (Fig. 2.12) illustrates, near equiatomic alloys without precipitates is found only in a narrow part of the phase diagram. Small variations in the concentration of Ni atoms produce different precipitates. For Ni-rich NiTi alloys, Ni_4Ti_3 and Ni_3Ti are found. In contrast, Ti-rich alloys show NiTi_2 precipitates. The NiTi_2 shape and

distribution in NiTi film depend on the temperature and time of annealing. Thin plate precipitates were observed when specimens were heat-treated below 820 K. Those precipitates were found to be effective for the stability of shape memory behavior at high temperatures⁴⁰. Above 820 K, spherical precipitates were observed in the parent phase. NiTi₂ was reported to have a face-centered cubic structure with a lattice parameter about four times larger than that of Ni-Ti. In films annealed at 600 °C, the precipitates had small round shapes and were homogenously distributed inside the grains. These particles are around 20 to 30 nm and have the same orientation with the austenite matrix⁴¹. However, the size of the precipitates increase with increasing heat treatment temperature: 30 to 150 nm in diameter at 970 K⁴⁰.

Fig. 2.12. Phase diagram of Ni-Ti alloy system³².

Chapter 3: Sample preparation and techniques of characterization

In this chapter, the techniques used to produce and characterize our samples, NiTi and NiTi/(Ni, Co) attached to Si(100), are described. We also discuss the relationship between the sputtering conditions and the features of NiTi alloys, as well as some literature on NiTi films having martensite phase at room temperature in attached films.

3.1. Film deposition process

3.1.1. Magnetron sputtering technique

Sputtering is a physical vapor deposition method widely used in the production of thin films⁴². Atoms are taken from pure solid targets and deposited in a substrate. The representation of a sputtering system with only one target is depicted in Fig. 3.1. For deposition, the chamber is filled with an inert gas, usually argon, which is ionized after hitting free electrons. Those electrons are accelerated away from the negatively charged electrode (cathode) by a potential difference applied in the gun, where the target is located in relation to the substrate, while the positive ions are accelerated and hit the target. As a result, target atoms and additional free electrons are released by energy transfer in the collisions. In a magnetron system, few magnets are located behind the cathode to trap the free electrons in a magnetic field directly above the target surface. Thus, these electrons continue ionizing the argon gas while others recombine with argon ions releasing energy in the form of photons. At equilibrium between these two processes, a confined plasma is created, and the released atoms are deposited onto the substrate.

Fig. 3.1. Left: Sputtering process in a system with one target. The argon ions are accelerated to the cathode and release target atoms and electrons in the collisions. Right: Plasma and magnetic field lines in a magnetron sputtering system⁴³.

In this research, NiTi films were deposited by DC co-sputtering of pure Ni and Ti targets in an ATC 2000 AJA International sputtering system. Four concentric guns (magnetrons) were assembled at the bottom of the main chamber, which has a capacity of approximately 90,000 cm³, while the substrate was localized at the top. Two lamps of 1000 W were located behind the substrate for heating. Prior to deposition, a high vacuum of the order of 10⁻⁶ Torr at temperatures above 550 °C was required to avoid any contaminants.

3.1.2. Overview of sputtering conditions of NiTi films used to observe the shape memory effect in attached NiTi films

NiTi films are generally deposited onto Si(100) single crystal substrates. To crystallize the films, they are treated for more than 0.5 hours at a high temperature. This crystallization process leads to a strong interaction at the interface between the substrate and NiTi film, which can severely diminish or inhibit the shape memory effect. To avoid the loss of effect, freestanding NiTi films are usually preferred. Those can be obtained using a thin sacrificial layer, such as Si₃N₄ or SiO₂. Polyimide and gold have also been reported as alternatives⁴⁴. For our purpose, we needed to preserve the shape memory effect in the NiTi film attached to the substrate. According to the literature, this effect is not completely suppressed in the films if the martensite phase is observed at room temperature, after cooling from the annealing step. This characteristic can be obtained by controlling the sputtering parameters to decrease the interaction at the interface with

the substrate and enable the austenite phase to transform into the martensite phase. Since the performance of these films is influenced by the sputtering conditions, such as co-sputtering with multiple targets, target power, argon gas pressure, target to substrate distance and deposition temperature, a brief overview of these conditions is provided in the following paragraphs.

In NiTi films, the shape memory effect is sensitive to the stoichiometry of the films; the highest effect is observed near the equiatomic composition. Such composition cannot be obtained by using only an equiatomic NiTi alloy target. Previous research proved that deposited films from a single target show a lower Ti concentration than Ni^{30,45} unless the NiTi alloy target were heated during deposition³⁰. This result was due to the difference in sputtering yield (number of atoms sputtered per Ar ion) of both atoms. Ni atoms have a higher sputtering yield than Ti atoms. Therefore, under the same applied power, more Ni than Ti atoms is deposited on the substrate surface. To compensate for Ti loss during sputtering, an additional supplier of Ti is needed unless we employ a Ti-rich NiTi target. The Ti supplier could be pure Ti discs⁴⁶ or chips²⁸ on the NiTi target surface. An alternative way to obtain equiatomic NiTi films is by working in the co-sputtering mode, where two targets with suitable powers are employed. These targets could be two different NiTi targets⁴¹, one NiTi target plus a pure Ti target^{27,38,47} or separately two pure Ni and Ti targets^{26,39}.

During the sputtering process, argon ions remove atoms from the target. However, argon atoms around the substrate could have a negative effect during the film deposition. Increasing the argon gas pressure in the main chamber restricts the Ni and Ti atoms diffusion on the surface. Miyazaki et al.²⁸ observed a columnar structure in the NiTi film deposited at high argon gas pressure. The diffusion of the deposited atoms is apparently restricted by the argon atoms near the substrate, producing this columnar structure or porous film. Another cause could be the low energy of the sputtered atoms after collisions with argon ions, limiting the surface diffusion. Both causes decrease the surface diffusion of Ni and Ti atoms on the surface. In contrast, a flat and featureless structure is obtained when working at low argon gas pressure. In Huang et al.⁴⁸, NiTi films were deposited at different argon gas pressures, from 2.3 to 20 mTorr. They observed a smooth and dense film surface only for a working pressure of 2.3 mTorr. Although usually this pressure is

below 2 mTorr, a wide range from 0.5 to 5 mTorr is believed suitable to obtain NiTi films without columnar structures²⁵.

Film microstructure seems also to depend on the kind of sputtering targets used. In Tillmann et al.⁴⁵, the microstructures of films deposited from separate elemental targets and a Ti-rich alloy target were compared. Both depositions were carried out at low argon gas pressure of approximately 2.63 mTorr. Films with continuous and fibrous microstructure were obtained by sputtering with the Ti-rich NiTi alloy target. In contrast, featureless and dense films with smaller amounts of well-crystallized material were obtained by co-sputtering elemental targets. The small quantity of crystallized material led to a lower shape memory effect, which is unwanted for our purpose. Moreover, choosing the right kind of target is important to avoid the Ti loss and obtain Ti-rich NiTi films. Otherwise, we would obtain Ni-rich NiTi films with the martensite transition start temperature below room temperature. Therefore, the columnar structure is not only due to a high argon gas pressure, as we discussed, but can also be obtained by using NiTi alloy targets. Although fibrous or columnar microstructure is favorable to the shape memory effect, dense and featureless films would have better mechanical resistance. Nevertheless, we need to be aware that a columnar structure is commonly obtained in sputtered films.

Another parameter affecting the energy flux of the sputtered atoms is the target-substrate distance. A large separation reduces the energy flux. However, there is a distance at which small variations in the separation do not have an important variation in energy. This distance is commonly reported between 2 and 5 cm²⁵. Higher values, such as 10 cm, have also been reported^{35,47}.

In summary, all the above-mentioned points indicate the microstructure of NiTi films is strongly related to the kinetic energy of the Ni and Ti atoms. The quantity of energy with which the atoms reach the surface is a crucial point for their diffusion and microstructure of the film in which parameters such as stoichiometry of the target, co-sputtering, argon gas pressure and target-substrate distance lead to a specific microstructure.

The next step, after achieving the equiatomic composition, is to crystalize the film to obtain the shape memory effect. As sputtered NiTi films are amorphous at room temperature, an annealing process or deposition at high temperature is required. The annealing time is not a standard value. Times varying from 0.5 to 4 hours have been reported at different annealing temperatures. However, the exposure time at high temperature must always be reduced to avoid increasing the interaction between the surface and the substrate to not lose the shape memory effect. As mentioned, the effect is observed in attached films if they display the martensite phase at room temperature. Previous research illustrating the martensite phase at room temperature in attached NiTi films are briefly presented in the following paragraphs. The sputtering conditions employed in these reports are summarized in Table 3.2.

Ho and Carman³⁰ deposited NiTi films with a rate of approximately 225 nm/min. They studied the effect of heating the target on the deposited films. In their research, three different processes were evaluated. The first used a cold target (C samples) as in a typical sputter deposition. In the second (sample T), the target temperature was modified during sputtering; temperatures were increased to > 700 °C. The third process (sample H) used a hot target > 400 °C. The researchers found a similar chemical composition between the deposited film and the target when the latter was heated (Table 3.1). The same relationship was also observed in the crystal structure depicted in Fig. 3.2. Additionally, they studied the effect of heating the substrate to 200 °C, 300 °C, 500 °C and 600 °C while using a cold target and found that the substrate heating did not produce martensitic films.

Table 3.1. RBS results of NiTi target and films deposited from a heated target (T sample), hot target (H sample) and cold target (C sample)³⁰.

Sample	Ni (at.%)	Ti (at.%)	Ni/Ti ratio
C sample	50.8	49.2	1.03
T sample	49.5	50.5	0.98
H sample	49.2	50.8	0.969
Target	48.2	51.8	0.931

Fig. 3.2. X-ray diffraction pattern of NiTi target (a) and the sputtered film from a heated target (T sample) (b), hot target (H sample) (c) and cold target (C sample) (d)³⁰.

Fu and Du³⁵ studied the effect of composition and annealing on the film stress during the shape memory effect. NiTi films were prepared by co-sputtering, from which the martensite phase was exhibited in films with a composition of 51.3% Ti. X-ray diffraction analysis of $\text{Ni}_{0.49}\text{Ti}_{0.51}$ films is illustrated in Fig. 3.3. For heating measurements, films were previously cooled below room temperature. Thus, when reaching room temperature, the films only had the martensite phase, as depicted in Fig. 3.3(b). It proves that under their sputtering conditions, the researchers obtained the martensite phase at room temperature in attached films.

Fig. 3.3. (a) X-ray diffraction analysis with change of temperature reveals the phase changes during the cooling process; (b) X-ray diffraction analysis during heating³⁵.

Fu et al.²⁷ researched the effect of thickness of NiTi films on the shape memory effect. $\text{Ti}_{50.2}\text{Ni}_{49.8}$ films with different thicknesses were prepared by co-sputtering without substrate heating. The XRD analysis of these films is illustrated in Fig. 3.4. The as-deposited films exhibited an increase in the martensite phase as the thickness increased. The researchers also observed that after cooling, the martensite phase increased. This result suggests that there is no a strong interaction between the film and the substrate. Otherwise, part of the austenite phase would not transform to martensite with the cooling process.

Fig. 3.4. X-ray diffraction patterns of NiTi films with different thicknesses after being cooled with liquid nitrogen vapor: (a) as-deposited films; (b) cooled with liquid nitrogen²⁷.

In Kumar et al.³⁷, different substrate temperatures were evaluated in the co-sputtering of NiTi films. The authors focused on the grain size effect on the NiTi film properties. Deposition was performed for 30 minutes at 623, 723, 823 and 923 K, and film compositions were 49.7%, 49.9%, 50.2% and 50.6% at%Ti, respectively. The researchers proposed that deposition at a temperature above the eutectoid point of the NiTi compound (903 K) facilitates the aggregation and growth of the small grains, which could be a reason NiTi films deposited at 923 K achieve the martensite phase at room temperature, as illustrated in Fig. 3.5.

Fig. 3.5. X-ray diffraction pattern of NiTi films deposited at 623 K, 723 K, 823 K and 923 K³⁷.

Sharma et al.⁴⁹ researched the influence of substrate temperature on the properties of the shape memory NiTi films. XRD analysis of $\text{Ni}_{0.49}\text{Ti}_{0.51}$ films deposited at 400 °C and annealed at different temperatures is depicted in Fig. 3.6. The highest percentage of martensite phase was found for films annealed at 500 °C. Furthermore, the rate of deposition was evaluated for films deposited at 300 °C and annealed at 600 °C. An increment in the martensite phase was observed as the current of the target increased. Both results suggest that the martensite phase depends on the substrate temperature and the deposition rate.

Fig. 3.6. X-ray diffraction patterns at room temperature of NiTi thin films deposited at 400 °C (AD) and annealed at 500 and 600 °C for four hours⁴⁹.

Koker et al.²⁶ studied the reverse martensitic transformation in NiTi shape memory alloys. Ni_{0.49}Ti_{0.51} films with 1.9 μm of thickness exhibited the martensitic phase at room temperature, as illustrated in the X-ray diffraction patterns (Fig. 3.7).

Fig. 3.7. θ -2 θ scans of the films at different temperatures ranging from 20 °C to 120 °C throughout the heating portion of the thermal cycle. The reflections belonging to the austenite (A) and martensite (M) phases have been indicated as well as those of the Ti₂Ni precipitates²⁶.

Kabla et al.³⁶ studied the relationship between the sputtering conditions and phase transformation temperatures in NiTi films of 3 μm . An interlayer of SiN was deposited on the silicon surface through chemical vapor deposition. Different phases of NiTi, unrelated to the chemical composition, were observed over all the films. These phases were associated with the difference in the grain size. X-ray diffraction analyses, illustrated in Fig. 3.8, indicated that the martensite phase appeared in matt regions of the films with a grain size of 200 nm, twice the size of that in the austenite region. Also, some critical grain size may be required to exhibit the martensite phase. It is believed that in sizes between 50 and 100 nm, the energy barrier for the martensitic transformation is so high that transformation is inhibited. Thus, the inhibition of the martensitic transformation is due to the small grain size of the particles and the strain constraint from the substrate.

Fig. 3.8. X-ray diffraction patterns of NiTi films (a) as-deposited, (b) taken from the matt region after annealing, (c) taken from the shiny region after annealing, and (d) same as (c) but focused on a small range of the intensity axis to observe the small martensite peaks³⁶.

Table 3.2. Sputtering conditions and thicknesses of films showing the martensite phase at room temperature. h: film thickness, d: Target-Substrate distance, T_{Sub} : Substrate temperature, T_{Ann} : Annealing temperature. t_{spu} : Sputtering time. t_{Ann} : Annealing time.

<i>Ref.</i>	P_{Base} (Torr)	P_{Ar} (mTorr)	d (cm)	Targets	Power (W)	h (μm)	T_{Sub} ($^{\circ}\text{C}$)	t_{spu} (h)	T_{Ann} ($^{\circ}\text{C}$)	t_{Ann} (h)
³⁰	$< 5 \times 10^{-8}$	2	4	NiTi	300	2,5 11 0,9			500	0,16
³⁵		2,3	10	NiTi, RF Ti, DC	300, (0,15,20)	5	450	10	--, 650	
²⁷	2×10^{-7}	0,83	10	Ni ₄₅ Ti ₅₅ , RF Ti, DC	400 70				650	1
³⁷	10^{-7}		5	Ni, Ti			450, 550,650	0,5		
⁴⁹				Ni ₄₅ Ti ₅₅		2	300-500		600	4
²⁶	$7,5 \times 10^{-9}$	0,98		Ni, Ti	45, 140	1,9		4,5	650	0,5
³⁶	10^{-7}	2	6,5	Ni ₄₈ Ti ₅₂		3			450	0,5

The sputtering conditions employed in the above reports are summarized in Table 3.2. From these reports, we inferred that the martensite phase at room temperature in attached films could be obtained by controlling the kinematics of the sputtered atoms and the temperature during the crystallization process. A low base pressure, less than 10^{-6} Torr, is required prior to deposition. Low argon pressure, around 2 mTorr, should be used to obtain a homogeneous deposition, and target-substrate distance can vary from 5 to 10 cm. To crystallize the films, two possible methods can be used. Deposition can be performed at room temperature followed by an annealing process at high temperature around 600 to 650 $^{\circ}\text{C}$. In this process, there is no standard value of annealing time. Times of half hour, one hour and four hours were reported. The second method consists of depositing at temperatures between 450 and 500 $^{\circ}\text{C}$, at which the annealing process can be avoided. If required, an annealing step is carried out for a short time at annealing temperatures in the range of 600 to 650 $^{\circ}\text{C}$. Therefore, deposition at low temperatures, less than 500 $^{\circ}\text{C}$, and post annealing at higher temperature for less than one hour is a suitable alternative. Although these

conditions were not exactly followed in the sample preparation described in this thesis, the reader should consider following them for future work.

3.1.3. Sample preparation of NiTi/(Ni, Co) heterostructures

For the sample preparation, NiTi films were deposited on Si(100) substrates by co-sputtering high purity Ni and Ti targets. Prior to deposition, targets (Ni, 100 W and Ti, 140 W) were pre-sputtered for ten minutes to remove oxides and contaminants from the target surfaces. Suitable DC powers were applied to each target to achieve similar deposition rates. Before heating the substrate, the base pressure was around 2×10^{-7} Torr and of the order of 10^{-6} Torr at the temperature of deposition. The substrate holder was kept rotating at 20 RPM during deposition to achieve uniform deposition, which was carried out at temperatures above the 500 °C using an argon gas pressure of 5 mTorr. Following the deposition, films were annealed in a vacuum in the main chamber for four hours at or above the deposition temperature, based on the work of Sharma and Mohan^{50 49}. After the annealing process, the heater was turned off and the films were kept in the main chamber for approximately 12 hours for cooling. Subsequently, a thin ferromagnetic layer of approximately 20 nm of Ni or Co was deposited onto the NiTi films. Finally, a 10 nm capping layer of Nb was deposited onto the films to prevent oxidation. Prior to deposition of Co or Nb, targets (Co, 100W and Nb, 200 W) were pre-sputtered for ten minutes to clean their surfaces. A schematic representation of the heterostructures is illustrated in Fig. 3.9.

Fig. 3.9. Schematic representation of NiTi/Ferromagnetic heterostructures deposited on Si(100).

3.2. Rutherford backscattering spectrometry

Rutherford Backscattering Spectrometry is a widely used technique to study the surface layer of solids. A non-destructive technique, RBS is used for the quantitative analysis of

elemental composition, thickness and depth profiles of thin solid films or solid samples with analyzed depths of approximately 2 μm . In this technique, the sample, also called target, is bombarded with ^4He ions ($^4\text{He}^+$) with energies below 4 MeV. The light ions penetrate the film and collide with the nuclei of the stationary heavier atoms of the film, and the energies of ions that are scattered backwards are analyzed. This backscattering is a result of Coulomb repulsion and is known as Rutherford scattering.

The analysis of RBS can be explained through classical analysis of two-body elastic scattering (Fig. 3.10). The ions are represented by particle 1, which has mass M_1 while the nuclei of the sample atoms are represented by particle 2 with mass M_2 . Using the conservation laws of energy and momentum, we can obtain an expression for the energy, E , of the scattered ions (Eq. 3.1 and Eq. 3.2, where v is the initial velocity of particle 1, and v_1 and v_2 are the velocity after collision of particle 1 and particle 2, respectively).

Fig. 3.10. Schematic representation of the collision between the $^4\text{H}^+$ ions (particle 1) with mass M_1 and the target (particle 2) atoms with mass M_2 . Z_1 and Z_2 are the atomic numbers of particles 1 and 2, respectively. E_0 is the initial energy of both particles. E_1 and E_2 are the energies after the collision of particles 1 and 2, respectively.

$$\text{Energy conservation: } \frac{1}{2}M_1v^2 = \frac{1}{2}M_1v_1^2 + \frac{1}{2}M_2v_2^2 \quad (3.1)$$

$$\begin{aligned} \text{Momentum conservation: } M_1v &= M_1v_1 \cos \theta + M_2v_2 \cos \phi \\ 0 &= M_1v_1 \sin \theta - M_2v_2 \sin \phi \end{aligned} \quad (3.2)$$

Thus, the energy of the ions after collision is as follows:

$$E_1 = E_0 \left[\frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_2 + M_1} \right]^2 \quad (3.3)$$

where $K = E_1/E_0$ is the kinematic factor. The number and the energy of the backscattered ions are collected with a solid detector localized at the scattering angle θ (for our measurements, it was fixed at 170° to optimize the mass resolution). This generates a spectrum of counts versus energy, representing the distribution of the atoms in the sample (Fig. 3.11). Using a computational program like SIMNRA, which was developed at the Max Planck Institute für Plasmaphysik⁵¹, we fit the spectrum and obtain information about the composition and depth distribution of the elements.

Fig. 3.11. Left: Scattering geometry. Right: Contribution of each isotope in each sublayer⁵².

To fit the spectrum, the quadratic deviation of the simulated spectrum from the measured data points, χ^2 , is minimized by varying the input parameters of the calculations:

$$\chi^2 = \sum_i \omega_i^2 (N_{exp}(i) - N_{sim}(i))^2, \quad (3.4)$$

where N_{exp} is the number of counts in the measured spectrum, N_{sim} the number of counts in the simulated spectrum, i represents either individual channels or channels regions, and w_i is the weight of each data point ($1/\omega_i = \sqrt{N_{exp}}$, for $N_{exp} > 4$). For fitting, SIMNRA uses the Simplex algorithm to find the best minimum χ^2 .

To simulate the spectrum, SIMNRA considers superimposed contributions from each isotope of each sublayer of the sample target. The contribution is convoluted with a Gaussian function $f = f(E, \sigma)$ with width σ^2 , where σ is the differential scattering cross section. Thus, the final contribution to the energy spectrum $S(E)$ from each isotope in each sublayer is given by the following equation:

$$S(E) = \int_0^\infty S_0(E') f(E', \sigma^2(E')) dE', \quad (3.5)$$

where S_0 and $S(E)$ are the energy spectrum before and after convolution, respectively. Thus, the number of counts N_i in each channel i is given by the integration of $S(E)$ over the channel E :

$$N_i = \int_{E_{\min}(i)}^{E_{\max}(i)} S(E') dE' \quad (3.6)$$

To calculate the contribution of each isotope in each sublayer, area Q in Fig. 3.11, the SIMNRA program uses the cross section at the main energy (Eq. 3.7). $N\Delta\Omega$ is the number of incident ions times the solid angle of the detector and $\sigma(\bar{E})$ is the differential cross section at main energy:

$$Q = N\Delta\Omega\sigma(\bar{E}) \frac{\Delta x}{\cos \alpha} \quad (3.7)$$

To be more precise, Q can be expressed in the integral space:

$$Q = \frac{N\Delta\Omega}{\cos \alpha} \int_{E_0}^{E_1} \sigma(E) \frac{dx}{dE} dE \quad (3.8)$$

Also, if dx/dE , called stopping power, is considered a constant S , then Q can be expressed as follows:

$$Q = \frac{N\Delta\Omega}{\cos \alpha} \frac{1}{S} \int_{E_0}^{E_1} \sigma(E) dE \quad (3.9)$$

In the RBS analyses of our samples, the measurements were carried out at two different energies, depending on the thickness of our films. $^4\text{He}^+$, with an energy of 2.2, and 4 MeV were employed to analyze films of 100 nm and 1 μm , respectively. The high energy was necessary in order that ion beam penetrates a deeper part of the substrate and thus increase the number of counts coming from it. Consequently, the substrate contribution to the spectrum was well resolved. To simulate the spectra, the following was considered: the stopping power data by Ziegler/Biersack, Rutherford cross section with the Anderson correction and energy-loss straggling model of Chu and Yang, which varies the width of the Gaussian function $f(E, \sigma)$.

3.3. X-ray diffraction

X-ray diffraction is a technique used to study crystalline structures based on the interference phenomenon of monochromatic X-rays. When an X-ray beam strikes a plane surface, interacting with the periodic array of atoms, their electrons can inelastically or elastically scatter the X-rays (Fig. 3.12). Crystal information is obtained from elastic scattering (i.e., where the beam wavelength is conserved). The scattered beam interferes constructively or destructively at specific angles producing a maximum or minimum intensity, respectively. Then, a pattern of intensities, also known as a diffraction pattern, is formed. The peak positions and intensities provide information about the crystal structure of the analyzed sample. The diffraction phenomenon obeys Bragg's law described by Eq. 3.10, where hkl are the Miller indices of the plane ($h k l$), d_{hkl} is the distance between adjacent planes ($h k l$), λ is the wavelength of the X-rays, θ is the angle of incidence and n is the reflection order. According to this equation, two or more scattered rays must be in phase in order to observe diffraction (i.e., a constructive interference). Therefore, the path difference between the incident and diffracted beams must be null or an integer multiple of the wavelength.

Fig. 3.12. Schematic representation of X-ray diffraction by a crystal.

$$2d_{hkl}\sin\theta = n\lambda ; \text{Bragg law} \quad (3.10)$$

In polycrystalline films, grains are randomly distributed, as is schematized in Fig. 3.13. To analyze its crystalline structure, a $\theta - 2\theta$ scan is extensively employed. This configuration is represented in the right of Fig. 3.13, where the sample is localized in the center of the sphere and the X-ray source is positioned at the θ angle relative to the plane surface while the detector collects the information at the 2θ position. With this symmetric arrangement, only planes parallel to the surface contribute to the Bragg reflections. Thus, the intensity of each diffracted peak is the contribution of grains with associated planes parallel to the surface.

Fig. 3.13. Left: X-ray diffraction for a polycrystalline thin film. Right: θ - 2θ scan of X-ray diffraction⁵³.

In X-ray diffraction, the term grain size or particle size refers to the size of small crystals (less than 100 nm) called crystallites. Generally, many of these crystallites form a particle in a crystalline sample, as depicted in Fig. 3.14. A crystallite should not be confused with the grains of crystalline samples, although sometimes they may be the same⁵⁴.

Fig. 3.14. Schematic diagram for grain size and crystallite of a crystalline powder⁵³.

In XRD patterns, the width of Bragg peaks is affected by the microstructural features like small crystallite sizes, crystallite shape, shape distribution and distortion of the crystal structure⁵³, as well as by instrumental factors like the divergence of incident beam or the width of the X-ray source. Without considering the instrumental broadening, the broadness of the Bragg peaks is mostly caused by the small grain sizes or, to be more precise, the crystallite size, which can be calculated using the Scherrer equation as follows:

$$t = \frac{0.9 \lambda}{B_{1/2} \cos \theta_B}, \quad (3.11)$$

where t is the diameter of crystallite size perpendicular to the plane, λ is the wavelength, θ_B is the Bragg angle and $B_{1/2}$ is the full width at half of its maximum intensity.

For our measurements, X-ray was generated by a Cu K $_{\alpha}$ anode ($\lambda = 1.5418 \text{ \AA}$). θ - 2θ scans were measured with angle step of 0.05° or 0.02° carried out using D8 Discover, Bruker equipment. The crystal phase identification of our samples was achieved using the MATCH software with the PDF 2003 as the base files of crystal structures. Additionally, to calculate the grain size of nickel in the heterostructures NiTi/Ni, grazing incident beam diffraction was carried out on 20 nm thick Ni on Si(100). In this configuration, the angle of incidence was 2.5° , and the scattered rays were collected in a range of 2θ . The small angle of incidence allowed us to see the grains along the surface, which improves the statistics of the counts.

3.3.1. Rietveld refinement

The Rietveld refinement is a mathematical method that calculates a diffraction pattern to fit experimental XRD pattern data, providing crystal structure information⁵⁵. To calculate the pattern, background, sample parameters (cell parameters, atomic positions and temperature factors), optical effects and instrumental factors are taking into account by the method. Briefly, the Rietveld refinement works minimizing the difference, S_y , between the calculated and observed pattern through the method of least squares as follows:

$$S_y = \sum_{i=1}^n w_i (y_i - y_{ci})^2, \quad (3.12)$$

where y_i is observed intensity, y_{ci} is calculated intensity, w_i is the weight of intensity ($w_i = 1/\sigma_i^2$) in point i and σ_i is the variance in point i . In this method, the calculated intensities are determined by the following:

$$y_{ci} = S_t \sum_k L_k |F_k|^2 \phi_{(2\theta_i - 2\theta_k)} P_k A + y_{bi}, \quad (3.13)$$

where S_t is the scale factor, k is the Miller indice, L_k is the Lorentz polarization function, ϕ is the reflection profile function, F_k is the structure factor for the k reflection, P_k is the preferential orientation function, A is the absorption factor and y_{bi} is the background in point i .

The fit is controlled by the numerical parameters, such as R_{wp} and R_{exp} :

$$R_{wp} = \left[\frac{\sum_{i=1}^n W_i (y_i - y_{ci})^2}{\sum_{i=1}^n W_i (y_i)^2} \right]^{1/2} \quad (3.14)$$

$$R_{exp} = \left[\frac{(N - P)}{\sum_{i=1}^n W_i (y_i)^2} \right]^{1/2}, \quad (3.15)$$

and the quality of the fit is determined by $\chi^2 = \left[\frac{R_{wp}}{R_{exp}} \right]^2$, as much the calculated pattern fits the real pattern the value of χ^2 is reduced. Although usually less than 2, this value is obtained only in patterns with narrow peaks. This was not the case in our analyses of NiTi layers, where the minimum values achieved were between 20 and 80.

In the analysis of Rietveld refinement by the FullProf software⁵⁶, the following input parameters were considered. Pseudo-Voigt function as the peak shape of the profile data. The background was fitted with a 2-coefficients polynomial function. Austenite and martensite phases had space groups of P m-3m and P 1 21/m 1, respectively. The group space of Ti₂Ni precipitates was 227 with Laue class m3m (Fd -3m). Atom positions information expressed as 'Element name (x, y, z)' was obtained with Powder Cell software: The atomic positions for austenite were Ni (0.5, 0.5, 0.5) and Ti (0, 0, 0). For martensite the atomic positions were Ni (0.0394, 0.2500, 0.2436) and Ti (0.4315, 0.2500, 0.7048), and for Ti₂Ni the positions were Ti₁ (0.311, 0, 0), Ti₂ (0.125, 0.125, 0.125), Ni (0.912, 0.912, 0.912). The occupancy number of Ni and Ti in austenite was 0.02083 and in martensite was 0.5. The occupancy number of Ti and Ni in Ti₂Ni was 0.05. Cell parameter: a, b, c and α , β , γ were 2.99, 2.99, 2.99 and 90, 90, 90 for austenite, 2.867924, 4.132999, 4.633451 and 90, 96.38, 90 for martensite and 13.6, 13.6, 13.6 and 90, 90, 90 for Ti₂Ni. Thermal parameters were fixed at 1.

There is no a defined sequence of fitting; however, in general, the parameters were fitted in the following order: Scale, background coefficients, cell parameters, width of reflections (U, V, W), peak shape parameters (eta, x) and atomic position. Usually, the three first parameters were selected to be fitted in any fit run. Initially, U and V were fixed to zero while W was fitted; then, we fit the U and V parameters.

3.4. Superconducting quantum interference magnetometer

A superconducting quantum interference magnetometer is highly sensitive equipment for measuring small variations of the magnetic flux, which are detected by using a superconducting quantum interference device (SQUID). This detector is a superconducting ring with one or two parallel-connected Josephson junctions in its path that detects small currents. In the first case, the detector is called RF SQUID, while in the second, it is DC SQUID. In a DC SQUID magnetometer, the magnetic moment of a sample is obtained by detecting magnetic flux changes through concentric coils (Fig. 3.15). This arrangement can measure the AC susceptibility and DC moment of a sample. In a DC measurement, the sample moves vertically through these coils, produces a change in magnetic flux and a current is induced circulating the coils. As illustrated in the schema, a small part of the coils system is in proximity to a SQUID detector. The induced

current circulating the coil system generates a change of magnetic flux through the ring, which induces a measurable current to circulate the ring to cancel the flux. Then, by measuring the voltage in the junctions, we obtain the magnetic moment of our sample.

The detection coil is a single-piece superconductor wire wound in a set of three coils configured as a second-order (second-derivate) gradiometer⁵⁷ (Fig. 3.15). The negatively charged upper and bottom coils are single turn, wound clockwise, and the positively charged center coil comprises two turns, wound counter-clockwise. In the recorded signal, the large middle signal is the reading from the center coil, while the smaller signals at the top and bottom are the readings from the upper and bottom coils, respectively. Thus, the geometry of the pickup coils defines the shape of the plot. This configuration is important because it eliminates interferences from nearby magnetic sources.

Fig. 3.15. DC SQUID detection schematic⁵⁸.

To carry out a measurement, the sample is firstly centered to ensure all the coils were detecting the magnetic moment of the sample. This step is completed by moving the sample upward in a full scan through the coils. The response of the SQUID detector to the magnetic moment of the sample during the scan is analyzed with a regression algorithm to center the signal by moving the sample according to the analysis. The sample is centered when the peak of the large, middle curve was within 0.05 cm of the half-way point of the scan length. In a 4 cm scan, as was our measurements, the sample was centered when the peak of the middle curve was within 0.05 cm

of the 2 cm point. Fig. 3.16 depicts a centered sample (square) positioned in the start point of the scan, one-half scan length before the center coils.

Fig. 3.16. A centered sample in the detecting coils of a SQUID magnetometer.

In our measurements, the sample was moved upward through the pickup coils along the scan length. The measurement response data of the sample was recorded after one scan. Thirty-two data points per scan were analyzed with a specific algorithm to compute the magnetic moment of the sample.

The magnetic behavior of our samples was analyzed by measurements of ZFC and FC curves with the magnetic field applied parallel to the film surface. To obtain a ZFC curve, the sample was firstly cooled without applying any magnetic field to reach the temperature in which the measurement began and a particular magnetic field was applied. Thus, the total magnetic moment was measured during the sample heating. The FC curve was subsequently taken during the sample cooling and is the measurement of the total magnetic moments in the presence of the applied field. A second measurement was also carried out after the FC measurement: the field cooled warming (FCW) curve recorded during heating. To study the temperature dependence of coercivity, magnetic hysteresis loops at different temperatures were measured in the bilayers, varying the applied external field from -30 to 30 kOe. Samples were initially cooled without any applied magnetic field to 10 K. Then, they were heated to the temperature at which the corresponding isothermal hysteresis loop was recorded.

Chapter 4: Chemical and structural characterization

In this chapter, the chemical composition and depth profile obtained by RBS analyses of films deposited at different temperatures (at 600 °C and below 600 °C) are presented. The structural characterization obtained by using XRD analyses, quantifying the crystalline phases via the Rietveld method, are also described.

4.1. Chemical characterization: Rutherford backscattering spectrometry

4.1.1. NiTi/(Ni, Co) heterostructures deposited at 600 °C

4.1.1.1. Calibration: Equiatomic NiTi films

To find the suitable powers of Ni and Ti targets to obtain NiTi films near their equiatomic composition through sputtering, five films were deposited at different powers for Ti, while the power for the Ni target was constant at 50 W. The thickness was expected to be around 100 nm based on the time of deposition, calculated by considering a deposition rate of 0.19 Å/s at 50 W and 0.18 Å/s at 125 W for the Ni and Ti target, respectively. Deposition was carried out at 600 °C, and the pressure in the chamber at this temperature and before deposition was 1.5×10^{-6} Torr. The RBS measurements were carried out at 2.2 MeV of 4He^+ , and the results are provided in Fig. 4.1. We observed that the equiatomic composition was obtained with powers of 50 W and 175 W for Ni and Ti, respectively. Therefore, we considered the relationship $P_{\text{Ti}}/P_{\text{Ni}} = 3.5$ a reference for the next deposition.

Fig. 4.1. RBS experimental (dots) and simulated (solid line) spectra for 100 nm of NiTi films deposited on Si (100) at different Ti powers (P_{Ti}).

Analysis of X-ray diffraction of the sample deposited at $P_{Ti} = 175$ W (Fig. 4.2) resulted in narrow peaks related to the substrate and a broad peak around 42° , indicating the amorphous structure of the film. This amorphous characteristic was also observed in films deposited without heating⁵⁰ and in films deposited at low temperature, such as 400°C ⁵⁹. Hence, we concluded that an annealing step was necessary to crystallize the films. Following the work of S. K. Sharma and S. Mohan^{50, 49}, the annealing of our samples was carried out in a vacuum at 600°C for a period of four hours.

Fig. 4.2. XRD pattern for 100 nm thick NiTi film deposited on Si(100).

4.1.1.2. NiTi/(Ni, Co) heterostructures

Four NiTi films of approximately $1\ \mu\text{m}$ thickness were deposited at different powers for the Ti target around the relationship $P_{Ti}/P_{Ni} = 3.5$. The power for the Ni target was kept constant at 100 W. The time of deposition was around three hours, calculated from considering deposition rates of $0.19\ \text{\AA/s}$ at 50 W for Ni and $0.18\ \text{\AA/s}$ at 125 W for the Ti target. Each deposition of NiTi (A, B, C, D) was divided into three groups: one was kept as NiTi, and on the other two, a thin layer of Ni or Co was deposited. As a result, we had NiTi, NiTi/Ni and NiTi/Co films for each Ti power.

Rutherford backscattering spectrometry simulated curves for NiTi films and the respective depth profiles are illustrated in Fig. 4.3. To fit the spectra, we considered the formation of $\text{Ni}_x\text{Ti}_y\text{Si}_{1-x-y}$ interlayers represented the compositional gradation through the film thickness as a consequence

of diffusion of atoms by being exposed at high temperature of 600 °C for a long period. Each spectrum is divided into three well-differentiated regions; the first, a wide plateau below 1800 keV, represents the substrate of Si(100), while the narrow peak at the right side is the capping layer of Nb. The mixture of plateaus in the region between 1800 keV and 3200 keV provides the information for the NiTi layer. The atomic percentage of Ti in the NiTi layer is around 50% in all groups, as listed in Table 4.1. This feature is one of the necessary conditions of NiTi to observe the SME. From the analyses of the depth profile, we obtained the thickness of the NiTi layer (see Table 4.1) and of the diffused region. The latter represents approximately 10% of the NiTi thickness. A larger diffusion region was observed for Group A monolayer in which NiTi has a thickness of 470 nm, represented between 370 and 2844×10^{15} atoms/cm² in the depth profile. However, large diffusion did not occur in the respective bilayers of Group A, hence we consider the diffusion in the monolayer as an independent effect. By using a NiTi density of 6.476 g/cm³, obtained from our post Rietveld refinement, we calculated that NiTi film of Group D had a thickness of 958 nm. According to Fu et al.²⁷, NiTi layers with a thickness of this order exhibit large variations in stress with temperature. This large recovery stress is needed to use NiTi as the actuator and modify the magnetic properties of ferromagnetic films in NiTi/(Ni, Co) due to the inverse magnetostrictive effect.

The RBS spectra and the simulated curves of NiTi/(Ni, Co) heterostructures are illustrated in Fig. 4.4, which also depicts the difference in the shape of each spectrum, between 1800 and 3200 keV, for different powers of the Ti target. The thin ferromagnetic layer of Ni or Co only represents a narrow peak in the spectra, around 3025 and 3040 keV, respectively. This narrow region, together with the noisy feature of the spectra, made it difficult to obtain an accurate value for thicknesses of the ferromagnetic layers. For this reason, the values listed in Table 4.1 differ from the 20 nm calculated prior to the ferromagnetic layer deposition.

Fig. 4.3. Left: RBS experimental (dots) and simulated (solid line) spectra for NiTi films of 1 μm deposited on Si(100) at different Ti powers. Right: Corresponding element distribution through the film thickness.

Fig. 4.4 RBS experimental (dots) and simulated (solid line) spectra of 20 nm thick of Ni and Co on NiTi films of 1 μm thick deposited on Si (100) at different Ti powers (P_{Ti}).

Table 4.1. RBS results: Atomic percentage of Ti, thickness (h_{NiTi} , h_{Ni} and h_{Co}) of NiTi, Ni and Co layers, respectively, in NiTi, NiTi/Ni and NiTi/Co films deposited at different powers of Ti target, P_{Ti} . To calculate each thickness, densities of NiTi, Ni and Ti were considered $\rho_{\text{NiTi}} = 6.476$, $\rho_{\text{Ni}} = 8.908$ and $\rho_{\text{Co}} = 8.9$ g/cm³.

Group	P_{Ti} (W)	NiTi/Ni			NiTi/Co			NiTi	
		Ti	h_{NiTi}	h_{Ni}	Ti	h_{NiTi}	h_{Co}	Ti	h_{NiTi}
		(at.%)	(nm)	(nm)	(at.%)	(nm)	(nm)	(at.%)	(nm)
A	330	49	863	7	49	863	7	51	470
B	340	52	894	6	52	892	6	49	893
C	350	53	858	10	53	859	10	50	881
D	360	52	979	7	52	982	7	52	958

To evaluate a possible contribution of oxygen in the chemical composition of the films, we chose the experimental spectrum of $\text{Ni}_{0.48}\text{Ti}_{0.52}/\text{Ni}$ of Group D and calculated the simulated spectrum with the additional element of oxygen in the NiTi layer. The fitting is illustrated in Fig. 4.5(a) and indicates a possible contribution of oxygen in the NiTi layer of less than 3%. However, this quantity is within the percent error of the composition, as depicted in Fig. 4.5(b), which indicates for variations up to 3% in the atomic composition, the simulated spectra continues to fit the experimental curve well.

Fig. 4.5. (a) Simulated spectrum of $\text{Ni}_{0.48}\text{Ti}_{0.52}/\text{Ni}$ of Group D considering a contribution of oxygen. (b) Evaluation of the limit in the Ti atomic percent to have similar RBS simulated (solid lines) spectra for $\text{Ni}_{0.48}\text{Ti}_{0.52}/\text{Ni}$ of Group D.

4.1.2. NiTi/Ni heterostructures deposited below 600 °C

NiTi films of approximately 1 μm thickness were deposited at different powers for the Ti target ($P_{Ti}/P_{Ni} = 3.56, 3.53$), while the power for the Ni target was kept constant at 100 W. Those relationships of P_{Ti}/P_{Ni} were chosen to obtain a similar composition of the sample of Group D (Section 4.1.1.2). The deposition time was around three hours, calculated by considering deposition rates of 0.38 $\text{\AA}/\text{s}$ at 100 W for Ni and 0.51 $\text{\AA}/\text{s}$ at 360 W for the Ti target. The temperature of deposition was 550 °C and 540 °C for Group I and Group II, respectively. All the films were annealed at 500 °C during four hours in a vacuum. Each deposition was divided into two subgroups in which part of the NiTi was used to prepare NiTi/Ni bilayers with a Ni thickness of approximately 20 nm, while the remaining NiTi was kept as reference.

The RBS spectra of the NiTi films and their respective depth profiles are depicted in Fig. 4.6. Although the relationship (P_{Ti}/P_{Ni}) employed to deposit the film was slightly less than the 3.6 used to deposit NiTi in Group D, the atomic percentage of Ti was higher than 52%. In addition to the high concentration of Ti, a large diffusion region was observed in the films deposited with $P_{Ti} = 356$ W (Group I), which is appreciable in the depth profile of Fig. 4.6. The diffusion region of Group I was rich in Ti indicating that the kinetic energy of Ti atoms were higher than Ni atoms, which agrees with the high atomic percentage of Ti observed in the NiTi layer. This result could be a consequence of employing a new Ti target since the rate of deposition in new targets is higher at the beginning of its use.

Fig. 4.6. Left: RBS experimental (dots) and simulated (solid line) spectra for 1 μ m thick NiTi films deposited on Si(100) at different Ti powers (P_{Ti}) and deposition temperatures (T_d). Right: Corresponding element distribution through the film thickness.

The RBS analyses of the Group I and Group II bilayers are illustrated in Fig. 4.7, in which two different pieces of Group II were also analyzed: NiTi/Ni (a) and NiTi/Ni (b). In Group I bilayer, we observed the expected diffusion region which was larger than for the monolayer. The bilayers of Group II, where NiTi was deposited with $P_{Ti} = 353$ W, displayed atomic percentages of Ti of 56% and 58%. However, the difference is within the error of 3% in the fit.

Fig. 4.7. Left: RBS experimental (dots) and simulated (solid line) spectra for $1\mu\text{m}$ thick NiTi/Ni films deposited on Si(100) at different Ti powers (P_{Ti}) and deposition temperatures (T_d). Right: Corresponding element distribution through the film thickness.

4.2. Structural characterization: X-ray diffraction measurements

4.2.1. NiTi/(Ni, Co) heterostructures deposited at 600 °C

The crystalline feature of the NiTi films was exhibited in all the XRD patterns, measured at room temperature. Fig. 4.8 reveals the NiTi layer is polycrystalline, displaying peaks of the martensite and austenite phases, as well as Ti_2Ni precipitates, which are known to provide stability to the shape memory effect at high temperatures. The difference between the patterns indicates that NiTi films have different crystal structures despite having similar chemical compositions. The predominant peak around 42.7° corresponds to the (110) lattice orientation of the austenite B2 structure. Since the austenite phase is formed at high temperatures, its presence at room temperature may indicate that the martensite transformation was not complete at this temperature. A second possibility is that the austenite was fixed due to the remaining stress at room temperature after the annealing step (i.e., residual stress). If the austenite was arrested due to residual stress, then it was not able to undergo the structural transformation. In contrast, the martensite phase at room temperature ensured the reverse martensitic transformation after heating.

Fig. 4.8. XRD patterns of 1 μm thick NiTi and the substrate measured at room temperature.

In relation to bilayers (Fig. 4.9 and Fig. 4.10), an interesting result was observed in Group D, where the austenite peak was suppressed after deposition of the Ni or Co ferromagnetic layer. This result suggests that the austenite phase of the NiTi layer was not as stable as in the other NiTi films. Furthermore, the result suggests that this film does not have a strong interaction with the substrate, which corresponds to the fact that the NiTi film from Group D had more peaks related to the martensite phase. The crystalline feature was also confirmed in all the bilayers.

Fig. 4.9. XRD patterns of 1 μm thick NiTi/Ni and the substrate measured at room temperature.

Fig. 4.10. XRD patterns of 1 μm thick NiTi/Co and the substrate measured at room temperature.

The indexation for NiTi film of Group D first was obtained by comparing different PDF files of the possible phases in the sample. The corresponding PDF file numbers used to index the pattern were 00-035-1281, 03-065-0537 and 01-018-0898, for martensite, austenite and Ti_2Ni , respectively. Then, a quantitative analysis was performed using the Rietveld method for all the NiTi layers in the 2θ range of 37° to 47° . The analysis for NiTi of Group D is illustrated in Fig. 4.11, where the largest peak at 42.7° represents the austenite phase (110), while the broad peak at 42.5° represents the amorphous phase in NiTi. From this analysis, we obtained the phase fractions of the austenite and martensite phases expressed in percentages, as well as the percentage of Ti_2Ni at room temperature. The percentages in this sample and the other groups are listed in Table 4.2. The percentages of the martensite phase in Groups A, B, C and D were 17%, 19%, 12% and 55%, respectively; the highest contribution of the martensite phase was obtained for Group D. The percentages of the austenite phase were 65%, 45%, 51% and 17% for Groups A, B, C and D, respectively; the austenite phase in Groups A, B and C represents approximately three times the value obtained for NiTi in Group D. Percentages of Ti_2Ni were 18%, 36%, 37% and 5% for Groups A, B, C and D, respectively. These precipitates cause intrinsic stress that increases residual stress³⁴. Thus, the lower percentage of Ti_2Ni in Group D implies a lower residual stress in NiTi film than in Group C.

Fig. 4.11. Rietveld analysis of the XRD pattern of NiTi film of Group D.

Table 4.2. Structural parameters of austenite (A), martensite (M), Ti₂Ni (T) and amorphous phase (am) of NiTi monolayer of Groups A through D extracted from the Rietveld refinement of the respective XRD patterns.

	Phase	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Weight (%)
Group A	A	2.99	2.99	2.99	90	90	90	65
	M	3.03	4.16	4.85	90	105	90	17
	T	11.31	11.31	11.31	90	90	90	19
Group B	A	2.99	2.99	2.99	90	90	90	45
	M	2.99	4.17	4.77	90	104	90	19
	T	11.32	11.32	11.32	90	90	90	37
Group C	A	2.99	2.99	2.99	90	90	90	51
	M	2.93	4.16	4.73	90	101	90	12
	T	11.29	11.29	11.29	90	90	90	37
Group D	A	2.99	2.99	2.99	90	90	90	17
	M	2.88	4.13	4.63	90	97	90	55
	T	11.28	11.28	11.28	90	90	90	5
	am	3	3	3	90	90	90	23

To observe the structural transformation, XRD measurements at different temperatures during cooling were performed on the NiTi film of Group D. Each recorded pattern was normalized by dividing the intensity data by the maximum intensity found in the pattern. The normalized patterns are displayed in Fig. 4.12(a) and were indexed using the Rietveld information presented in Fig. 4.11. From each pattern, the percent area under the peaks was calculated by fitting the peaks with the Lorentzian function. The evolution with temperature of the percent area under each peak is given in Fig. 4.12(b). The simultaneous decrease of the austenite phase A(110) percentage and the martensite phase M(020) increment as the temperature decreases proves the martensitic transformation was carried out.

Fig. 4.12. XRD analyses of NiTi film of Group D at different temperatures during cooling, A: Austenite, M: Martensite and T: Ti_2Ni . (a) XRD patterns with normalized intensity. (b) Evolution of each peak area with temperature.

Grazing incidence XRD on 10 nm thick Ni on Si(100) was measured to calculate the Ni grain size. The pattern is illustrated in Fig. 4.13 in which a Gaussian fit was performed to obtain the width value at half of the peak intensity. Using this value and the respective Bragg angle in the Scherrer equation (see Eq. 3.11), a grain size of 10 nm was obtained.

Fig. 4.13. Grazing incidence X-ray diffraction of 20 nm thick Ni deposited on silicon.

4.2.2. NiTi/Ni heterostructures deposited below 600 °C

The XRD patterns of NiTi films of Group I and Group II where NiTi was deposited at 550 °C and 540 °C, respectively, are displayed in Fig. 4.14. The patterns were similar between groups and exhibited crystalline features even though the temperatures of deposition were below 600 °C. The angle range representing the crystalline phases of NiTi was between 37° and 47°. The peaks around the austenite phase A(110) at 42.7° were associated with the martensite phase and the Ti_2Ni precipitates. The XRD analyses of the bilayers are illustrated in Fig. 4.15; the fractions of austenite and martensite phases in the region between 37° and 47° were different than in the respective NiTi monolayers (Fig. 4.14). This difference in Group I may be a result of the low residual stress in the NiTi layer that makes part of the austenite transform to martensite during Ni deposition, which is the stable phase of NiTi at room temperature. In both the monolayer and bilayer patterns, we observed a peak at 40.7°, which requires further analysis to understand.

Fig. 4.14. XRD patterns of 1 μm thick NiTi measured at room temperature. Austenite (Δ), Substrate (S), Martensite (M), and Ti_2Ni (T).

Fig. 4.15. XRD patterns of 1 μm thick NiTi/Ni measured at room temperature. Austenite (Δ), Substrate (S), Martensite (M), and Ti_2Ni (T).

Chapter 5: MAGNETIC PROPERTIES:

Magneto-elastic coupling in NiTi/(Ni, Co) heterostructures

In this chapter, the magnetic behavior of the Ni and Co ferromagnetic films is studied in NiTi/(Ni, Co) heterostructures through the structural phase transition of NiTi. Magnetization as a function of temperature and field are analyzed for two kinds of heterostructures in which NiTi was deposited at two different temperatures.

Prior to addressing the magnetic behavior of heterostructures with 1 μm thick NiTi, we briefly illustrate the absence of the magnetic-elastic effect in NiTi/(Ni, Co) heterostructures when NiTi thickness is 100 nm. To this purpose, 100 nm thick NiTi films were deposited at 600 $^{\circ}\text{C}$ and annealed at the same temperature for four hours. After cooling the NiTi film, 20 nm of Ni or Co was deposited on the NiTi surface. Thus, we obtained $\text{Ni}_{0.50}\text{Ti}_{0.50}/\text{Ni}$ and $\text{Ni}_{0.48}\text{Ti}_{0.52}/\text{Co}$ heterostructures deposited at 170 W and 175 W for the Ti target, respectively, while the power for the Ni target was kept constant at 50 W.

Magnetic measurements for the bilayers were carried out in a vibrating sample magnetometer. Prior to the measurements, the bilayers were submerged into a bath of liquid nitrogen in order to begin the measurement from the martensite phase. The curves of magnetization as a function of temperature are depicted in Fig. 5.1. In fact, the curves recorded during heating were not exactly ZFC curves. It is due to the magnetic field was only applied when the sample reached the room temperature, which may cause that a FC curve goes down a ZFC as it was observed for NiTi/Co

heterostructure. In both bilayers, we observed the decrease of magnetization during heating, characteristic of ferromagnetic materials. There were no additional anomalous characteristics indicating the presence of a magneto-elastic effect.

Fig. 5.1. Total magnetic moment as a function of temperature under an applied magnetic field of 500 Oe for 100 nm thick of NiTi in NiTi/Ni and NiTi/Co bilayers.

Magnetic hysteresis loops at two different temperatures are depicted in Fig. 5.2 for both bilayers. Since it was reported that the austenite phase starts around 60 °C, one hysteresis was carried out at this temperature and the other at a lower temperature to be in the martensite phase. For the measurement, the maximum applied external field was 4 kOe. Fig. 5.2 illustrates that neither the coercivity nor the hysteresis shape changed with temperature for either bilayer. Since no magnetic change was observed, we concluded that a magneto-elastic effect is not exhibited in bilayers with 100 nm thick NiTi. Additionally, from the hysteresis loops we obtain the coercivity of 54 Oe and 170 Oe of the ferromagnetic layer in Ni_{0.50}Ti_{0.50}/Ni and Ni_{0.48}Ti_{0.52}/Co, respectively.

Fig. 5.2. Magnetic hysteresis curves at different temperatures for 100 nm thick NiTi in NiTi/Ni and NiTi/Co bilayers.

We attributed the absence of the magneto-elastic effect to the thin thickness of the NiTi layer. As mentioned in Section 2.3, the shape memory effect is barely observed in films with thicknesses less than 200 nm due to the oxide layer formed on the top of the film and the inter-diffusion layer between the film and the substrate becoming dominant, restricting the phase transformation. In contrast, a great recovery stress for thicknesses higher than 800 nm was reported. Therefore, the following films in this research had a thickness around 1 μm .

5.1. NiTi/(Ni, Co) heterostructures deposited at 600 °C

Curves of magnetization as a function of temperature were measured for all bilayers of Groups A, B, C and D. Before addressing the magnetic behavior of the ferromagnetic layer in the heterostructures, we evaluated the magnetic contribution of the NiTi layer. To find the NiTi contribution, ZFC and FC curves of NiTi monolayers attached to the substrate were measured in the range of temperatures from 10 K to 380 K. The results for the NiTi films from Groups C and D are displayed in Fig. 5.3. Both samples during the thermal cycle had a low magnetic moment with a magnetic behavior characteristic of paramagnetic materials because, practically, there is no variation in the magnetic moment with temperature. Therefore, the NiTi layer does not affect the magnetic behavior of the top ferromagnetic layer. The negative value of the total magnetic moment comes from the diamagnetic contribution of the massive substrate Si(100). The irreversible behaviors shown by the magnetic moment at low temperatures, both in Group C and D, suggest the existence of a small magnetization originating in the rough surface of the NiTi.

Fig. 5.3. Total magnetic moment as a function of the temperature for 1 μm thick NiTi films of Groups C and D. The measurements were carried out under an external field of 500 Oe.

The magnetic response of the ferromagnetic layer to the temperature was analyzed by measuring ZFC and FC curves of Ni film deposited on Si(100), illustrated in Fig. 5.4. The Ni film was deposited under the same conditions as the deposition of the Ni layer in the heterostructures. The dimensions of the sample of Si/Ni were larger than the NiTi/Ni from Group A through D. At the beginning of the ZFC, thermal energy was supplied to the system for the first time, and spins gained mobility to align with the field. Above 80 K, the aligned spins also tried to align adjacent spins and highly increased the total moment in a short range of temperatures. After the spin alignment, the total moment decreased with temperature. Since the grain size of Ni (10 nm, see Fig. 4.13) was below the critical size of magnetic monodomain for Ni, we saw each grain as a magnetic monodomain with the blocking temperature (T_B) taken at the maximum point of the ZFC. Therefore, T_B was 250 K for Ni film (Fig. 5.4) and by using Eq. 2.4, we determined the effective anisotropy constant of Ni is $K_{effNi} = 16.47 \times 10^4 \text{ J/m}^3$. This value is one order of magnitude higher than the anisotropy constant reported for Ni bulk $0.57 \times 10^4 \text{ J/m}^3$ ⁶⁰ due to the contribution of shape anisotropy in films. However, the K_{effNi} is of the same order of magnitude when it is compared with the constant anisotropy of 15 nm thick Ni film deposited on Cu(001), $5 \times 10^4 \text{ J/m}^3$ ⁶⁰.

Fig. 5.4. Zero field cooled (ZFC) and Field cooled (FC) curves of 20 nm thick of Ni on Si(100) under an in-plane applied magnetic field of 100 Oe.

Fig 5.5 depicts ZFC and FC curves for $\text{Ni}_x\text{Ti}_{1-x}/\text{Ni}$ bilayers of Groups A through D. In Group D, the FC start above the end point of the ZFC curve because the thermal instability of the straw. During sample heating, ZFC, the magnetization of Ni gradually increased with temperature. This behavior was due to thermal energy supplied to the system increased the spins mobility and the spins align in the direction of the magnetic field. The next faster increase in the magnetization is attributed to the interaction between neighboring spins; aligned spins try to align with neighboring spins. The threshold of temperature where this interaction occurs was above 270 K for bilayers of Groups A and B; for bilayers of Groups C and D, it occurred above 130 K. The complete alignment of spins with the external magnetic field of 100 Oe was obtained at blocking temperature T_B . For the bilayers of Groups A, B, C and D, T_B was at 332 K, 320 K, 300 K and 285 K, respectively. The higher values of blocking temperature in the bilayers than the blocking temperature (250 K) for the Ni monolayer indicates an increase of the effective anisotropy constant, $K_{eff\text{NiTi/Ni}} > K_{eff\text{Ni}}$, as a result of the induced anisotropy stress. Using Eq. 2.4 and the volume of each Ni crystallite ($V_{\text{Ni}} = 524 \text{ nm}^3$), the $K_{eff\text{NiTi/Ni}}$ for each bilayer was computed and is exhibited in Table 5.1. After the spin alignment, the magnetization of ferromagnetic materials was expected to gradually decrease with additional thermal energy to become null at the Curie temperature; however, a clear additional increase of the magnetization was observed in the

bilayers with Ni (inset of Fig. 5.5(a), (b), and (d), indicated by *). For Group A, the enhancement occurred after a fast loss of the moment due to temperature (inset of Fig. 5.5(a)). For Group C, we believe the additional enhancement began before the complete spin alignment, which was again observed later by a fast decrease in its coercivity. In all the bilayers with Ni, the clear enhancement observed was not a feature of ferromagnetic films, and since the measurement was performed at a constant magnetic field, the magnetic field could not cause the additional increase of the moment; hence, we infer that the anomalous enhancement of magnetization is due to an interaction between the Ni and NiTi layer.

By considering addition of anisotropies, the stress anisotropy constant, K_σ , can be seen as the difference between the effective anisotropy constants between the bilayer and the Ni monolayer, $K_{\sigma_{NiTi/Ni}} = K_{eff_{NiTi/Ni}} - K_{eff_{Ni}}$, in which we considered the anisotropy constant of Ni on Si(100) to be the same as for the Ni film on NiTi. By using the relationship for the stress anisotropy constant, $K_\sigma = \frac{3}{2}\lambda_{si}\sigma$, the interfacial stress for each group was computed and is presented in Table 5.1. The values of the stress given by the NiTi layer are in agreement with the order of stress in previous reports²⁷.

Fig. 5.5. Zero field cooled (ZFC) and Field cooled (FC) curves of NiTi/Ni of Groups A, B, C and D under an in-plane applied magnetic field of 100 Oe.

Table 5.1. Blocking temperature, T_B obtained graphically from the ZFC curve of the bilayers. Effective anisotropy density constant, $K_{eff\text{NiTi/Ni}}$, for NiTi/Ni films computed using Eq. 2.4. Stress anisotropy constant for NiTi/Ni films $K_{\sigma\text{NiTi/Ni}}$, obtained by $K_{\sigma\text{NiTi/Ni}} = K_{eff\text{NiTi/Ni}} - K_{eff\text{Ni}}$ and $K_{\sigma} = \frac{3}{2}\lambda_{si}\sigma$.

Group	T_B (K)	$K_{eff\text{NiTi/Ni}}$ (10^4 J/m^3)	$K_{\sigma\text{NiTi/Ni}}$ (10^4 J/m^3)	$\sigma_{\text{NiTi/Ni}}$ (MPa)
A	332	21.88	5.41	1061
B	320	21.08	4.61	903
C	304	20.03	3.56	692
D	285	18.78	2.31	453

The additional enhancement observed in the bilayers with Ni was not observed in the bilayers with Co (Fig. 5.6(a), (b) and (c)). Although, for the bilayer with Co of Group D, displayed in Fig.5.6(d), the enhancement apparently occurred at 275 K, we cannot affirm it as an enhancement because the small variation in the magnetization between the beginning of the ZFC and the end of the FC curve. In the NiTi/Co bilayers, ZFC and FC curves were always separated, showing irreversibility, indicating the blocking temperature of the Co is higher than the maximum temperature of the experiment. This fact can also be observed in the ZFC and FC curve for 20 nm thick Co deposited on Si(100), Fig. 5.7. Additionally, we observed that for all groups, the magnetic moment of the NiTi/Ni bilayers is highly sensitive to the interaction of the ferromagnetic layer with the NiTi layer in contrast to NiTi/Co bilayers. This is consistent with the results observed by De la Venta et. al¹³. The higher magnetization of saturation, M_s , and lower saturation magnetostriction constant, λ_{si} of Co compared to Ni induce higher stress anisotropy (Eq. 2.7) in bilayers with Ni.

Fig. 5.6. Zero field cooled (ZFC) and Field cooled (FC) curves of NiTi/Co of Groups A, B, C and D under an in-plane applied magnetic field of 100 Oe.

Fig. 5.7. Zero field cooled (ZFC) and Field cooled (FC) curves of 20 nm thick of Co on Si(100) under an in-plane applied magnetic field of 100 Oe.

For Group D, the ZFC and FC curves for the bilayer with Ni (Fig. 5.5(d)), the additional enhancement of the magnetization had its maximum at 320 K followed by a sharp drop in magnetization with heating. The temperature range in which the magnetic enhancement occurred was consistent with the temperature reported for the formation of the austenite phase in attached NiTi films to silicon substrate^{26,27,36,37}. This agreement was also supported by a four-wire resistance measurement in an attached Ni_{0.48}Ti_{0.52} film, confirming the range of transformation temperatures of austenite (Fig. 5.8). Hence, we attributed this behavior to interfacial strain between the ferromagnetic and NiTi layer during the reverse martensitic transition of NiTi. In contrast to the bilayer with Ni of Group C (Fig. 5.5(c)), there was a local minimum around 260 K during cooling (FC curve, Fig. 5.5(d)). This peak may be related to the intermediate R-phase observed in some Ti-rich NiTi alloys, relaxing the stress in two steps²⁶.

Fig. 5.8. Electrical resistance versus temperature curve of the Ni_{0.48}Ti_{0.52} film deposited at 550 °C. M_s , M_f , A_s , A_f , R_s and R_f are the martensite, austenite, and R-phase transition start and finish temperatures, respectively.

An additional thermal cycle recording the magnetization was completed for the NiTi/Ni bilayer of Group D, confirming the reversibility of the magneto-elastic coupling (Fig. 5.9). The starting point of the FCW lied below the first FC curve because the FCW was recorded 12 hours after finishing the first FC curve. The changes in the magnetization with temperature were again observed during heating (FCW) and cooling (second FC) the sample. The enhancement in the

magnetization shifted to 335 K, while the peak during cooling was observed at the same temperature (260 K) as the first FC. This recursive magnetic behavior with thermal cycle is a consequence of the reversible characteristic of the structural phase transition of NiTi.

Fig. 5.9. Left: Zero field cooled (ZFC), Field cooled (FC) and Field cooled warming (FCW) curves of NiTi/Ni of Group D under an in-plane applied magnetic field of 100 Oe. Right: Zoomed left figure.

Isothermal magnetic hysteresis loops were measured for NiTi/Ni of Group C and NiTi/(Ni, Co) of Group D, respectively (Fig. 5.10(a), (b) and (c)). These two groups were selected due to the large difference between the percentages of the martensite phase in their structures since this phase would certainly show SME. Group C was representative of Groups A and B because the martensite phase percentages were close among them, while in Group D, 55% was martensite phase, three times the value observed in the others. The magnetic loops were recorded during heating and around the temperature range where the anomalous enhancement in magnetization was observed. All the loops were symmetric, conserving their shape in the range of analyzed temperatures.

Temperature dependence of the hysteresis loops for NiTi/Ni of Group C is illustrated in Fig. 5.10(a). According to this figure, the magnetization at 100 Oe is $0.7 M_s$ while the remanent magnetization is approximately $0.58 M_s$. From these loops, the coercivity values were extracted

and are plotted in Fig. 5.10(d). The coercivity starts at 92 Oe at 240 K and constantly decreases with temperature to 63 Oe at 360 K (Fig. 5.10(d)). The coercivity at 300 K is 75 Oe, lower than the value of 140 Oe reported for 20 nm of unstressed Ni film electrodeposited onto substrates of CuSn_6 ⁶¹, and higher than the coercivity of 54 Oe for bilayer (100 nm thick NiTi)/Ni, Fig. 5.2(a). The difference in the coercivity could arise from the residual stress of NiTi attached to the silicon substrate. In contrast to the coercivity for the bilayer (100 nm thick NiTi)/Ni, the coercivity for the bilayer of Group C drops 9% between 300 K and 330 K. A fast decrease in coercivity was observed between 280 and 300 K, which was related to the small bump observed in the respective ZFC curve (inset of Fig. 5.5(c)).

Hysteresis loops for the NiTi/Ni bilayer of Group D are depicted in Fig. 5.10(b). Remanent magnetization is approximately $0.57 M_s$ for all the loops, similar to the NiTi/Ni bilayer of Group C. The temperature dependence of coercivity of Group D is represented in Fig. 5.10(e). This bilayer had slightly lower coercivity values than bilayer of Group C. At 300 K the coercivity has the same value than the coercivity for the bilayer (100 nm thick NiTi)/Ni, Fig. 5.2(a). Additionally; this bilayer shows a minimum of coercivity at 330 K, representing a relevant variation of 31% in relation to the coercivity at 300 K. This result agrees with the enhancement in the magnetic moment at 335 K observed in the FCW during the second thermal cycle (Fig. 5.9). After this point, a recovery of the coercivity was observed. Fig. 5.10(c) illustrates the hysteresis loops for NiTi/Co of Group D. Lower values of coercivity were observed for NiTi/Co than for NiTi/Ni of Group D. Now, in contrast to the coercivity of 170 Oe for the (100 nm thick NiTi)/Co bilayer, the coercivity for the NiTi/Co sample of Group D was 24 Oe at 300 K. The remanent magnetization was around $0.54 M_s$ for temperatures lower than 340 K and decreased to $0.44 M_s$ at 360 K. For this bilayer, the temperature dependence of coercivity resulted in a minimum at 340 K, and after this point the coercivity started recovering. Also, a decrease in magnetic moment at zero magnetic field can be observed in Fig. 5.10, mainly in the bilayer with Co. This behavior is related to the magnetic viscosity of the ferromagnetic layer which is much pronounced for bilayer with Co because its higher coefficient of magnetic viscosity.

Fig. 5.10. (a), (b), (c) In-plane hysteresis loops measured at different temperatures and (d), (e), (f) temperature dependence of the coercivity for the bilayers.

The magnetic behavior illustrated in Fig. 5.9 can be described as follows. During heating, the martensite phase in NiTi gradually transforms into the austenite phase, increasing the tensile stress on NiTi surface²⁷. Assuming this stress is uniformly distributed in all directions on the Ni

layer, we decompose the in-plane tensile stress in two directions, parallel and perpendicular to the applied in-plane magnetic field, and treat each of them as the sum of uniaxial stresses distributed in the respective lateral sides of the Ni layer. Furthermore, we know that stress can induce an easy axis of magnetization, reducing the magneto-elastic energy described by Eq. 2.6. For $\lambda_{si}\sigma < 0$, the axis is a hard axis and the plane normal to the stress becomes an easy plane. Therefore, as Ni has a negative magnetostriction constant and $\sigma > 0$ (tensile stress), the induced easy axes are perpendicular and parallel to the in-plane field when the stress is parallel and perpendicular to the field. Thus, the magnetization is favored by the increase of the stress perpendicular to the field, explaining the unusual enhancement with temperature. The maximum magnetization is then associated with a minimum coercivity.

5.2. NiTi/Ni heterostructures deposited below 600 °C

Magnetization as a function of temperature of NiTi/Ni of Group I and Group II is displayed in Fig. 5.11. For Group II, the two samples NiTi/Ni (b) and (a) were analyzed. In both groups, the blocking temperature is higher than the 250 K for 20 nm thick Ni film, in agreement with the bilayers of Groups A through D. Also, the anomalous increment of the magnetization associated with the formation of the austenite phase during heating was observed. In the FC curves, the minimum in the magnetization was exhibited in both groups, but with different shapes of the minimum between them. Therefore, we affirm the magneto-elastic coupling in heterostructures deposited below 600 °C.

In the bilayer of Group I, the anomalous increment of the magnetization during heating had the maximum at 356 K. For Group II, the maximum in the magnetization was observed at 360 K and 345 K for samples (b) and (a), respectively. In Group II, despite both samples being prepared under the same conditions, the magnetic response to the temperature was different between them. This result suggests that the microstructure of NiTi is relevant to reproduce the magnetic response. Moreover, we associate the differences in the shape of the peaks between samples in Group I, II and A through D to the morphology and crystal structure of the NiTi layer as it was observed for V_2O_3 /Ni bilayers with different roughness at the interface⁶².

Fig. 5.11. Zero field cooled (ZFC), Field cooled (FC) and Field cooled warming (FCW) curves of NiTi/Ni of Group I and Group II under an in-plane applied magnetic field of 100 Oe.

To determine how the magneto-elastic coupling in these heterostructures affects the coercivity of the ferromagnetic layers, magnetic hysteresis loops were measured at different temperatures (Fig. 5.12). The shape of the hysteresis loops was the same for all the bilayers. From the hysteresis loops, the coercivity was extracted and plotted, illustrated on the right side of Fig. 5.12. For Group I, further measurements at higher temperatures are required to determine whether, at the observed 360 K, the maximum in the magnetization had a minimum coercivity. For Group II, a smooth minimum was noticed in the coercivity at temperatures at which the maximum in the magnetization was observed: at 360 K and 345 K for samples (b) and (a), respectively.

Fig. 5.12. Left: In-plane hysteresis loops measured at different temperatures. Right: Temperature dependence of the coercivity for bilayers of Group I and Group II.

Chapter 6: Conclusions

Stress coming from the structural phase transition of NiTi with temperature enables the control of magnetic properties of the Ni and Co films in NiTi/(Ni,Co) heterostructures. In such heterostructures, the stress modifies the magnetization and coercivity of ferromagnetic films due to the inverse magnetostrictive effect. This magneto-elastic coupling is evidenced by an anomalous enhancement in the magnetization of the ferromagnetic layer with temperature. Moreover, in-plane magnetic hysteresis loops had a fast decrease in the coercivity when magneto-elastic coupling occurred.

Tensile stress at the interface during the structural phase transition of NiTi induces an easy axis of magnetization in the ferromagnetic layer to reduce the magneto-elastic energy, explaining the anomalous enhancement in the magnetization.

The NiTi/Ni heterostructures proved to be more sensitive to the magneto-elastic coupling than NiTi/Co. Also, the largest response was observed in $\text{Ni}_{0.48}\text{Ti}_{0.52}/\text{Ni}$ of Group D in which NiTi crystal structure had a high percentage of the martensite phase at room temperature: 55%.

To summarize, the signature of magneto-elastic coupling in the NiTi/Ni heterostructures, anomalous enhancement in the magnetization with temperature, is illustrated in Fig. 6.1 for NiTi/Ni of Group D and Group II, in which NiTi layers have a high percentage of the martensite phase at room temperature. Our findings are of interest for controlling magnetism in films above room temperature and without applying an external field.

Fig. 6.1. Magneto-elastic coupling in NiTi/Ni heterostructures: Field cooled warming (FCW) and Field cooled (FC) curves, obtained at 100 Oe, for NiTi/Ni bilayers of Group D and Group II.

Outlook

- ❖ Study the stress evolution of NiTi with temperature focusing on the stress direction in the grains at different temperatures by XRD using an area detector.
- ❖ Performing out-plane magnetic measurements through the SPT of NiTi.
- ❖ Study the influence of roughness of NiTi in the magneto-elastic coupling.

Participations in schools/conferences

1. 62nd Annual Conference on Magnetism and Magnetic Materials. Pittsburgh, PA, USA, 2017.
 - **Diana L. Torres** and Daniel R. Cornejo. Magnetoelastic coupling in Ferromagnetic/NiTi heterostructures driven by structural phase transition. **(Poster)**.
2. XVI Brazilian Materials Research Society meeting. Gramado, Brazil, 2017.
 - **Diana L. Torres** and Daniel R. Cornejo. Inverse magnetostrictive effect in Ferromagnetic/NiTi/Si(100) heterostructures controlled by temperature. **(Poster)**.
3. 8th Joint European Magnetic Symposia. Glasgow, UK, 2016.
 - **Diana L. Torres** and Daniel R. Cornejo. Magnetoelastic effect in ferromagnetic/NiTi bilayer films attached to Si (100) substrate. **(Oral)**.
4. 6th School of transmission electron microscopy. Campinas, Brazil, 2016.
 - **Diana L. Torres** and Daniel R. Cornejo. Relation between the crystal structure interfaces of NiTi/Ni and FeRh/Fe films with their magnetic behavior. **(Poster)**.
5. Soft Magnetic Materials Conference - SMM22. Sao Paulo, Brazil, 2015.
 - **Diana L. Torres** and Daniel R. Cornejo. Study of the effect of the structural phase transition of NiTi on the magnetic properties of NiTi/Co and NiTi/Ni films. **(Poster)**.
6. Sao Paulo School of Advanced Science on Recent Developments in Synchrotron Radiation. Campinas, Brazil, 2015.
 - **D. Torres**, F. Garanhani, K. Montero, F. Aliaga, G. Pessotto, P. Badilla and D. Cornejo. Research on the magnetic behavior of multilayer and nanowire structures. **(Poster)**.

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