"Size effects in thin film Nickel-based alloys for (N)MEMS applications"

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“A theory is something nobody believes, except the person who made it.
An experiment is something everybody believes, except the person who made it.”

Albert Einstein
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Summary

The goal of this work was to study the influence of reduced dimensions (size effects) on phase composition and microstructural properties of metallic alloys. In particular, this research was focused on the effects of thermal treatments in two metallic systems used in nanotechnological applications. Sub-micrometric metallic films are nowadays widely used in many industrial fields, especially where the core technology relies on the extreme miniaturization of processes and components. It has been observed that, when one or more of the external dimensions of the physical system are reduced below the micrometer range, most materials develop unusual properties, compared to their bulk counterparts, due to the much increased surface/volume ratio and to the microstructural constraints offered to various physical phenomena by the interfaces of the material. The increased surface/volume ratio amplifies all the phenomena linked to the interactions of the material with the external environment (external environment or substrate) such as increased heat exchange rates or increased chemical reactivity while an example of microstructural constraint is the mechanical strengthening due to dislocation pinning by grain boundaries or by interfaces. Although some of these effects were initially considered as unexpected technological problems, the new and unexplored properties of materials in reduced dimensions are now seen as a great opportunity for an uncountable number of applications in a wide variety of fields like electronic, sensing, micro- and nano-robotics, pharmaceutical and biomedical industry, optics and power
generation/storage. Alloying is a powerful way of engineering micro and nano-sized metallic materials especially using production techniques allowing the manipulation of materials down to the molecular/atomic level such as: physical and chemical vapor deposition, molecular beam epitaxy, flame synthesis and wet chemistry based processes. The use of these techniques allows the production of materials with composition and microstructure virtually unknown to the traditional metallurgy. Due to the fact that specific research on this class of materials is a relatively recent field, few binary and ternary metallic systems in reduced dimensions have been explored up to date and no complete understanding of some aspects (crystallization, texture, phase formation, solid state precipitation, etc...) has still been reached. The metallic systems for this research have been chosen within the materials used in the production of micro- and nanoelectromechanical systems (MEMS, NEMS); the first system is the ternary Ni-Ti-Cu alloy used as intrinsic actuating material, thanks to its shape memory effect, and the second system is the Ni-W binary alloy, a high-strength material for miniaturized structures, typically patterned by means of X-Ray lithography, and for applications ranging from room temperature up to 1000 K (components for microturbines, solid fuel cells, catalysts, etc). This research project was carried out using a combinatorial approach, allowing the parallelization and automation of production and characterization techniques. The results show that the film thickness modulates the phase composition and the texture of the materials, especially in the presence of metastable phases, as clearly shown in the case
of the ternary Ni-Ti-Cu system. In these materials the austenitic-premartensite-martensite sequence is defined not only by the elemental composition and by the heat treatment, but also by the film thickness. It was also shown how minute shifts in the Cu contents of the films resulted in variations of texture width and even in crystallographic distortion of the austenite/premartensitic phase, due to the progressive substitution of Ti and Ni atoms in the original cell. The cooling rate after the annealing dramatically influenced the final crystallographic structure and phase composition of the films. In the Ni-W binary system, the second material object of this work, the effects of heat treatments and alloying in a wide range of compositions were studied. It was shown that a moderate heat treatment (800 K for 1 h) produces a softening in the Ni-rich alloys (grain growth) and a marked hardening of the W-rich alloys. These observations lead to the conclusion that two different hardening mechanisms exist in this kind of alloys: the Hall-Petch strengthening and the intermetallic phase formation. It has been found that the first mechanism is predominant in the range of composition 0<W<25 at%, while for the W richer alloys, the presence of intermetallics is the primary cause of hardening. Another important finding is that for the mentioned heat treatment, all the equilibrium phases are formed but not in the equilibrium phase composition. The third result of this work is the establishment of two experimental techniques in the field of thin film technology: a vacuum quenching device and a X-Ray diffraction method to characterize phase composition and texture of films. The first technique consists in a liquid
cooled flat plate installed inside a high-vacuum chamber (equipped with IR heater and used as an annealing furnace for thin films), that allows the quenching of the samples by means of contact cooling. This quenching method was used in the study about Ni-Ti-Cu alloys and it proved to have a determinant influence on the phase composition, crystallography and microstructure of the films. The second technique we introduced is used to characterize crystallographic features in potentially textured thin films using X-Ray diffraction. It consists in the repetition at different inclinations ($\psi$ angle) of the usual $\theta/2\theta$ scans, using a standard diffractometer equipped with a Eulerian cradle. From the theoretical point of view, this is an already known experimental configuration in crystallography as it can be seen as a "section" of the orientation distribution function of the material system in exam, but in practice it has been never extensively used in the study of thin films. In fact, throughout all the scientific literature reviewed during the preparation of the present research, only single $\theta/2\theta$ scans were encountered in the XRD characterization of thin films. In the case of a mixture of different and possibly textured phases, using a single XRD scan on a plain orthogonal to the surface of the sample (zero $\psi$ inclination) it is very likely to miss some peaks or to have a strongly altered peak intensity distribution, which may lead to a completely wrong interpretation of the phase content of the specimen. The pole figure method is based on a similar principle (diffraction scan around two different angular axes) but its use is not comparable with that of the method we propose. Although a pole figure contains a more detailed information
about the crystallographic orientation of a determined phase, it is unpractical to determine the phase composition of a textured sample. Under this point of view, the two methods can be considered complementary.
Riassunto

Lo scopo di questo lavoro è lo studio dell’influenza delle dimensioni ridotte (effetti di scala) sulla composizione di fase e sulle proprietà microstrutturali delle leghe metalliche. In particolare, questa ricerca è focalizzata sugli effetti dei trattamenti termici in due sistemi metallici usati in applicazioni nanotecnologiche. I film metallici sub-micrometrici sono al giorno d’oggi largamente usati in molti campi industriali, specialmente nelle tecnologie basate sull’estrema miniaturizzazione di processi e componenti. È stato osservato che, quando almeno una delle dimensioni fisiche del sistema si riduce sotto il micrometro, i materiali mostrano proprietà inusuali rispetto alle loro controparti massive a causa dell’elevato rapporto superficie/volume e a causa dei vincoli microstrutturali offerti dalle interfacce del materiale a diversi fenomeni fisici. L’elevato rapporto superficie/volume amplifica tutti i fenomeni derivanti dalle interazioni del materiale con l’ambiente esterno (ambiente esterno o substrato) come ad esempio maggior scambio termico o maggiore reattività chimica, mentre un esempio di vincolo microstrutturale è dato dall’indurimento causato dall’ostacolo al movimento delle dislocazioni da parte di interfacce o bordi grano. Anche se alcuni di questi effetti furono inizialmente considerati come inattesi problemi tecnologici, le nuove e inesplorate proprietà dei materiali a scale micrometrica e nanometrica sono al momento viste come una grande opportunità in innumerevoli applicazioni in un gran numero di campi come ad esempio in elettronica, sensoristica, micro- e nanorobotica, farmacia, biomedica, ottica, generazione e
immagazzinamento di energia elettrica. L’alligazione è un potente mezzo di
ingegnerizzazione per materiali in scala micro- e nanometrica specialmente
nel caso di processi di produzione che permettono la manipolazione dei
materiali a livello atomico/molecolare come: deposizione fisica o chimica da
stato vapore (PVD, CVD), epitassia da fasci molecolari (MBE), flame
synthesis e processi chimici in soluzioni (acquate e/o solventi organici). L’uso
di queste tecniche permette la produzione di materiali di composizione e
microstruttura virtualmente sconosciute alla metallurgia tradizionale. Dato
che la ricerca specializzata su questa classe di materiali è un campo
relativamente recente, a tutt’oggi pochi sistemi binari e ternari in scala micro-
e nanometrica sono stati esplorati e solo una parziale comprensione degli
aspetti di interesse (cristallizzazione, tessitura, formazione delle fasi,
precipitazione, etc...) è stata raggiunta. I sistemi metallici oggetto della
presente ricerca sono stati scelti fra i materiali usati nella produzione di
sistemi micro- e nanoelettromeccanici (MEMS, NEMS); il primo sistema è la
lega ternaria Ni-Ti-Cu usata come materiale attuatore intrinseco, grazie
all’effetto memoria di forma, e il secondo sistema è la lega binaria Ni-W, un
materiale a alta resistenza meccanica per strutture miniaturizzate,
tipicamente prodotte per mezzo di fotolitografia ai raggi X, e per applicazioni
da temperatura ambiente fino a 1000 K (componenti per microturbine, celle a
combustibile, catalizzatori, etc...). Questo progetto di ricerca è stato condotto
usando un approccio combinatoriale che ha permesso la processazione in
parallelo e l’automazione della produzione e della caratterizzazione dei
campioni. I risultati mostrano che lo spessore dei film modula la composizione di fase e la tessitura dei materiali, specialmente in presenza di fasi metastabili, come mostrato chiaramente nel caso del sistema ternario Ni-Ti-Cu. In questo materiale la sequenza austenite-premartensite-martensite è definita non solo dalla composizione elementare e dalla storia termica ma anche dallo spessore del campione. È stato anche evidenziato come minime variazioni nel contenuto di Cu nel film risultino in differenze nella distribuzione della tessitura e addirittura in una distorsione cristallografica della fase austenitica/premartensitica, a causa della progressiva sostituzione degli atomi di Ti e Ni della cella originale. La velocità di raffreddamento dopo il trattamento termico ha influenzato drasticamente la struttura cristallografica e la composizione di fase dei film. Nel sistema binario Ni-W, il secondo materiale oggetto di questo lavoro, sono stati studiati gli effetti di trattamenti termici e alligazione in un'ampia gamma di composizioni. È stato evidenziato che un trattamento termico di moderata intensità (800 K per 1 h) produce una riduzione della durezza nel caso di leghe ad alto contenuto di Ni e, al contrario, un marcato indurimento nelle leghe ricche di W. Queste osservazioni portano alla conclusione che esistono due diverse cause di indurimento in questa famiglia di leghe: l'effetto Hall-Petch e la formazione di fasi intermetalliche. Abbiamo dimostrato che il primo meccanismo è predominante nell'intervallo di composizione 0<W<25 at% mentre per leghe maggiore contenuto di W la presenza di intermetallici è la causa primaria di indurimento. Un'altra scoperta importante è che a seguito del menzionato
trattamento termico, tutte le fasi di equilibrio del sistema binario Ni-W sono presenti, ma non nei rapporti di composizione attesi secondo il diagramma di equilibrio. Il terzo risultato di questa ricerca è rappresentato dallo sviluppo di due tecniche sperimentali specifiche per il campo dei film sottili: un dispositivo di tempra ad alto vuoto e un metodo di diffrazione ai raggi X utile a caratterizzare composizione di fase e tessitura di film. La prima tecnica consiste in una piastra raffreddata a liquido installata all’interno di una camera ad alto vuoto (fornita di un riscaldatore a infrarossi e usata come fornace per trattamenti termici), che permette la tempra dei campioni per mezzo di scambio termico per conduzione. Questo metodo di tempra è stato usato nello studio delle leghe Ni-Ti-Cu dove è stata dimostrata la sua influenza sulla composizione di fase, sulla cristallografia e sulla microstruttura dei film. La seconda tecnica, basata sulla diffrazione ai raggi X (XRD), introdotta in questa ricerca è stata usata per caratterizzare proprietà cristallografiche in film con potenziale orientazione preferenziale dei grani di una o più fasi. Questa tecnica consiste nella ripetizione a differenti inclinazioni (angolo $\psi$) delle tradizionali scansioni angolari $\theta/2\theta$, usando un normale diffrattometro equipaggiato con una culla euleriana. Dal punto di vista teorico, questa configurazione sperimentale non è nuova in cristallografia dal momento che può essere vista come una “sezione” della funzione di distribuzione delle orientazioni del materiale in esame, ma in pratica questa configurazione non è mai stata utilizzata in maniera estensiva nello studio dei film sottili. In effetti, in tutta la letteratura scientifica esaminata
durante la preparazione della presente ricerca, solo scansioni singole \( \theta/2\theta \) sono state impiegate per la caratterizzazione XRD di film sottili. Nel caso di miscele di fasi diverse con possibile tessitura cristallografica, l’uso di scansioni XRD singole in un piano ortogonale alla superficie del campione (inclinazione zero dell’angolo \( \psi \) ) potrebbe facilmente portare alla perdita totale di alcuni picchi di diffrazione o quantomeno a uno sbilanciamento sensibile dei loro rapporti di intensità, risultando in un’interpretazione completamente errata della composizione di fase del campione. Il metodo delle figure polari è basato su un principio simile (diffrazione con scansione intorno a due diversi assi angolari) ma il suo uso non è comparabile con quello del metodo da noi proposto. Anche se la figura polare contiene una quantità di informazione superiore riguardo l’orientazione cristallografica di una determinata fase, è di dubbia applicabilità per determinare la composizione di fase di un campione con possibile orientamento cristallografico preferenziale. Da questo punto di vista, i due metodi possono essere considerati complementari.
1 Introduction

1.1 Motivation

The progress in miniaturization originated in the early stages of electronic and information technology industry has now extended its reach to many other industrial fields and the amount of consumer products containing nano-engineered components is growing at an extremely fast pace. The most promising fields of application of nanotechnologies are extremely diverse and range from electronics and information technology to life science, pharmaceutical industry, power generation, environmental technologies, just to cite a few. One of the most interesting sectors where micro and nanosized technologies have already shown an impressive potential is represented by the Micro and Nano Electro-Mechanical Systems engineering (N-MEMS), and a world-wide research effort is devoted to the development of new miniaturized machines that could be used in uncountable applications. An example of existing and effective product based on MEMS technologies is represented by the Digital Light Processing (DLP) projector based on Digital Micromirror Devices (DMD), both technologies being developed and patented by Texas Instruments at the end of the 80’s. This technology, currently leading the market of image projectors, is based on a chip, Fig. 1.1, composed of an array of millions of micrometer sized mirrors, Fig. 1.2, produced by means of photolitographic techniques.
Fig. 1.1: DLP chip, property of Texas Instrument.

Fig. 1.2: Detail of the DMD with two micro-mirrors removed to show the electromechanical structure, property of Texas Instrument.
The mirrors, suspended in a 3D structure composed of torsion springs and actuating electrodes are used as single pixel switches for incoming light to reproduce a high-definition digital image. Mechanisms of similar (and in the future, smaller) sizes are under development for a virtually infinite range of applications, and one of the most research intensive topics for this purpose is devoted to solve material aspects specific to the problematics and the needs of miniaturized systems. The main motivations of the research about materials in reduced dimensions come from two main considerations. First, when one of the external dimensions of the system is reduced to a legth below the micrometer, surfaces and interfaces start interacting with the material in a significant way, e.g. constraining dislocation motion (hardening effect) or influencing diffusion or heat transfer abilities of the material (crystallization, phase formation and grain growth); second, the fabrication methods used in nanotechnologies allow to manipulate composition and microstructure of the material in an unprecedented way, e.g. using physical vapor deposition techniques to produce alloys which are of practically impossible realization using the methods of traditional metallurgy (melting, mechanical alloying, etc.). Examples of these alloys are W-Mg or Pt-Mg, useful in the field of micro- and nanoporous materials produced by means of de-alloying, where the low-melting element would evaporate at the melting temperature of the high-melting element, making impossible the alloying in the liquid state. The physical differences between “bulk” and “nano” materials
result in a completely new world of properties rendering the traditional knowledge in materials science a mere starting point in the path to the complete understanding of the nano-sized materials. The present work is dedicated to the investigation of new metallic and intermetallic materials for mechanical applications for micro- and nano- machines. In particular, the effects of small dimensions and thermal history on the composition, microstructure and mechanical properties of metallic alloys in the shape of sub-micrometric films produced by means of magnetron sputtering were studied.

1.2 Thesis outline

The thesis starts with an overview about the metallic alloys chosen for this study, the film production techniques and the characterization procedures, followed by a main section composed by three full length articles. The first article describes the setup for the X-Ray diffraction (XRD) analysis of thin films that was used throughout the rest of this research. This technique overcomes the limitation of the traditional XRD scans over one single angular coordinate, which may result in the masking of important part of the signal in the case of textured films. Although conceptually similar, this technique is not equivalent to the pole-figure representation, which is rather aimed to the characterization of the statistical orientation of grains composed of a well defined phase. Moreover, compared to the single coordinate ($\theta/2\theta$) scans,
this technique allows the calculation of residual stresses and grain geometry of the films. The second article is based on the metallurgical characterization of Ni-Ti-Cu ternary shape memory alloy in the shape of thin film. Its focus is about the role played in the microstructure and crystallography of the materials by film thickness and thermal treatments. The effects of alloying and thermal treatments are also the topics of the third article which studies the mechanical properties of Ni-W binary system, again in the form of thin film, over a wide compositional range (W: 0-85 at%). In the final chapter, conclusions coming from the study of both metallic systems are drawn and some guidelines for future work are proposed.

1.3 Fabrication techniques

All the films object of this research were produced in the Physical Vapour Deposition facilities at ETH/FIRST Labs using a PVD Products [1] custom designed Magnetron Sputtering device, Fig. 1.3. This piece of equipment was specifically designed to allow the deposition of films with compositional and thickness gradients, allowing the realization of combinatorial research in this field. Combinatorial research consists in the study of films where one or more property are varied along one or two physical coordinates on the surface of one single sample, enabling high-throughput, automatized measurements that in other experimental conditions would require a much higher number of samples, and therefore time, to be completed.
The magnetron sputtering device installed in the FIRST Labs, ETH Zürich, can be considered the main instrument used for this work. This piece of equipment was designed to allow a high level of flexibility for depositing a wide range of materials and to accommodate many in-situ instruments for the production and the characterization of thin films. The specific configuration of this tool allowed the use of up to three magnetrons and therefore up to three different “target” materials. Magnetron sputtering is a versatile method allowing the vaporization of a wide range of materials by means of mechanical energy transfer from an ionized gas accelerated towards a target of the desired composition using an electromagnetic field. In Fig. 1.4 is reported a schematic of the system in its simplest implementation showing its main components.

Fig. 1.3: The magnetron sputtering device used for this work, courtesy of PVD Products and ETH/FIRST.
In a sputtering deposition equipment, a vacuum chamber encloses the active parts of the system and allows the deposition in a controlled atmosphere. It is fundamental to perform the deposition with a complete control: 1) over the partial pressure of the residual atmospheric gas in order to avoid unwanted chemical reactions during the deposition, and 2) over the pressure of the plasma-generating gas, to be able to tune the erosion dynamics of the target and the in-flight interactions of the atmosphere with the eroded material directed to the substrate. It would be also possible to introduce a partial pressure of a reactive gas during the sputtering procedure, to induce controlled chemical reactions with the eroded material (in-flight or on the surface of the sample) so to produce films with a different composition than the targets (e.g. oxydes, nitrides), nevertheless, this option was never used in our work. The principal active component in the sputtering process is the sputtering gun, where the target material is held in position inside the electric
field generated by a anode-cathode system and eroded by a plasma produced using the same electric field. The sputtering plasma is generated from the ionization of a gas, in our case Ar, introduced in the vacuum chamber and kept at a determined pressure during the whole deposition process by regulating a gate-valve positioned between the chamber and the vacuum pump. The sputtering pressure, usually in the range of 0.1 to 2 Pa, is an important process parameter because not only is it responsible for the sputtering plasma density and energy, but it also contributes to determine the energy of the sputtered material arriving to the substrate surface (by means of in-flight collisions) as described elsewhere [2, 3]. In the case of conductive materials the cathode is constituted by the target material itself, while for non-conductive materials, the cathode is the gun head, isolated from the anode and supporting the target. Compared with the system just described, the “magnetron gun” is a more advanced sputtering device, sketched in Fig. 1.5. It derives its name from the magnetic field that acts together with the mentioned electric field to confine and densify the sputtering plasma in a toroidal region above the surface of the target, therefore increasing the efficiency of the whole process. The magnetic field is produced by an array of permanent magnets situated below the target plate.
Fig. 1.5: Sketch and picture of a DC magnetron gun with the main components: 1) anode, 2) target material and cathode, 3) plasma, 4) permanent magnets. In the picture on the right the side, the corresponding elements are marked.

The sample preparation also included high temperature treatments and quenching in high vacuum, using equipment and procedures that were entirely developed by the author of this work. It is worth to mention that, due to the extremely reduced thickness of the films, oxidation and other unwanted chemical reactions with the atmospheric gases during a high temperature annealing represent a serious problem and may cause significant alterations of the samples. Only the use of special cautions and specialized high vacuum equipment can allow the heat treatment on these systems. In particular, a contact cooler for 3” wafers was designed, produced and installed in the high-vacuum chamber of the sputter tool to allow the quenching of the samples, after their heat treatment, without breaking the vacuum, as shown in Fig. 1.6 and 1.7.
Although very simple in its concept, an experimental set-up of this kind to perform high-vacuum annealing and quenching of complete wafers for combinatorial purposes is not commercially available and, at least to our knowledge, has never been used for combinatorial metallurgical studies with materials in the shape of thin film. Under this point of view, this work is pioneer in the understanding of the thermokinetics in the crystallization and phase formation of metallic alloys in the shape of thin films.
Fig. 1.7: Picture of the contact cooler developed by the author of this work. The cooled plate is supported by a vacuum tight motion feedthrough that allows its positioning inside the chamber.

1.4 Characterization

The analytical methods used in this work include electron imaging (SEM, TEM) and diffraction, ionic milling (FIB) and mechanical testing (Nanoindentation). Moreover, to overcome the limits of traditional X-Ray diffraction (XRD) when used on potentially textured films, the use of a special XRD procedure has been proposed and successfully used throughout this study. The technique we used is not new in terms of theoretical background [4], but its use for the characterization of thin films was applied only a handful of times in literature [5, 6] and never to study alloying or thermal treatment effects in reduced dimensions. This technique is object of the second chapter.
of this work, where complete descriptions of the experimental setup and data processing techniques are given. During our research, we realized that traditional, single scan, X-Ray diffraction was inadequate to characterize alloyed thin films due to the fact that the likely texture of one or more phases would cause the absence of characteristic peaks or a strong alteration of their relative ratios, hindering the correct determination of the phase composition of the samples. An example of this possibility is given in Fig. 1.8 where the same sample was studied using a single scan and a multiple-tilt scan. It could be objected that for a wide enough angular range in a simple $\theta/2\theta$ scan, even for highly textured samples at least one of the peaks should be visible. Nevertheless, in the case of special experimental setups (e.g. monocapillary lenses) where the accessible angular range is limited, the proposed multi-tilt ($\theta/2\theta$ vs $\psi$) analysis should be preferred. In any case, even where a classic $\theta/2\theta$ scan is feasible, the amount of additional information that this technique allows to extract is in our opinion already sufficient to justify the longer measurement times and extra effort in data processing that the multi-tilt analysis requires. Aside from the experimental techniques, a special mention should go to the role of information technology in this study. In the framework of combinatorial analysis, which is extensively used in this work, it is of fundamental importance to couple the use of automated measurement techniques with adequate data analysis software programs.
Fig. 1.8: Example of the difference between a classic XRD $\theta \rightarrow 2\theta$ scan (b) and multiple-tilt scan (a,c) on a textured thin film. The peak related to the TiNi austenite is completely absent in the classical setup.
The significant amount of information produced by position sensitive analyses like nanoindentation or focused XRD would be heavily underexploited if not processed in an automated way. Under this point of view, the highly specialized nature of this research required a considerable effort for the development of custom made software to perform calculations, statistical evaluation and display of the available data, coming from a range of equipment having each a different output-file standard. We bring as an example the construction of the determination of the Hall-Petch effect for a ternary alloy. In this case, a combinatorial thin film sample with a two dimensional elemental composition gradient was probed with a 6 x 6 measurement matrix to determine the variation of elastic modulus as a function of elemental composition. Every nanoindentation spot was tested 10 times with a multiple-depth (7 steps) indentation procedure, to evaluate the variation of the mechanical properties as a function of the indentation depth (surface/substrate influence). To properly analyze and display the data, a program was written so to perform the following operations: 1) loading the nanoindentation data from the corresponding files, 2) elimination of data exceeding reasonable pre-determined boundaries, 3) fitting of Elastic Modulus – Depth data curves following established models, 4) determination of E for every curve at a pre-defined indentation depth (h_i), 5) averaging of the resulting values (E_i), 6) loading the XRD (2θ/ψ) data, 7) fitting the peaks within defined angular boundaries (representative of a certain phase), 8) applying the Scherrer method to the fitting coefficients to estimate the grain
size of the phase, 9) combining the results of the nanoindentation characterization with the corresponding results of XRD-Scherrer grain size analysis, 10) plotting the two sets of data in logarithmic plot, 11) fitting the data in the logarithmic plot to determine the slope of the data distribution to prove the Hall-Petch dependence of Hardness vs Grain Size. This particular data processing flow is sketched in Fig. 1.9.

1.5 Materials

The material systems analyzed in this study were chosen because of their microstructural properties, making them suitable for a broad range of possible applications in the construction of micro- and nano-devices. The first system, TiNiCu ternary alloy, is the most promising material for micro and nano mechanical actuators due to its very high work/volume ratio at relatively high speeds of actuation. Its working principle relies on the thermally activated martensitic/austenitic phase transformation which can revert a deformed element made by this material to its undeformed shape. This property earned this alloy the name of “Shape Memory Alloy” (SMA) although under certain conditions, these materialy can show other equally intriguing properties like superelasticity and superplasticity.
Although much experimental and theoretical literature has been produced at this regard, the complexity of the involved phenomena make it still impossible to predict \textit{a priori} the behavior of a SMA alloy knowing its composition, microstructure and stress state. If this is true for bulk materials, in the microscopic realm of thin films the problems are multiplied due to the effects of reduced dimensions. Increased surface/volume ratio, reduced grain sizes, textured films, exceptionally high stress states are only a few of the “extra” parameters that can influence the microstructure and the properties of SMA.
thin films compared to their bulk counterpart, often producing unexpected effects in their thermomechanical behavior. Concerning the Ni-Ti-Cu system, the results of minor additions (<10 at%) of Cu to quasi-equiatomic Ni-Ti alloys were investigated. The alloying of Ni-Ti with Cu is very interesting in the field of microactuation because of the reduction of the thermal hysteresis in the martensitic transformation causing the shape memory effect. In the absence in literature of a complete ternary diagram for the Ni-Ti-Cu system, in Fig. 1.10, the binary diagram for the Ni-Ti system is shown.

Fig. 1.10: Binary diagram for the Ti-Ni system (Source: ASM International).

The Ni-W system, the second to be studied in this work, is a promising candidate for high strength, highly ductile films which can be used for the realization of Micro Electro Mechanical Systems (MEMS), typically produced
by means of the LIGA\(^1\) forming techniques. In particular, this alloy is considered an interesting material for high temperature applications in the field of MEMS. The reason behind the uncommon thermo-mechanical properties of this alloy mainly resides in the extremely reduced grain size that occurs when the W content of the alloy is around 20-25 at\%. Moreover, for compositions above 25 at\% W, the presence of many intermetallic phases modulates the microstructure and therefore the mechanical properties of the system. A broad compositional range (W 0-85 at\%) was investigated in both as deposited and annealed state to study the properties of films with higher W contents and, therefore, with potentially improved mechanical properties at high temperature. In Fig. 1.11 the equilibrium binary phase diagram for the Ni-W system is reported.

![Fig. 1.11: Binary diagram for the Ni-W system (Source: ASM International).](image)

\(^1\) LIGA is a German acronym for Lithographie, Galvanof ormung, Abformung (Lithography, Electroplating, and Molding) that describes a fabrication technology used to create high-aspect-ratio microstructures using X-Ray lithography.
1.6 References

[1] PVD Products IAS, Wilmington, MA 01887, United States of America.


2 Rapid Qualitative Phase Analysis in Highly Textured Thin Films by X-Ray Diffraction


2.1 Abstract

Phase analysis of highly out-of-plane textured specimens using X-ray diffraction is usually complicated due to the disappearance of most of the X-ray peaks in a common $\theta/2\theta$ diffraction geometry. In this paper, we propose a technique, where powder-like spectra of textured samples are obtained by multi-axial X-ray diffraction scans. This technique is a simple, yet powerful method which allows for significant improvement in thin film characterization and provides several types of information about the samples, such as the rapid qualitative identification of phases using common powder X-ray diffraction spectra databases, texture distribution and quantitative residual stress analysis.

2.2 Introduction

Metal thin films in the sub-micron range usually exhibit strong out-of-plane textures due to the minimization of interfacial energies [1]. Natural materials
such as sea shells may show an anisotropic oriented assembly due to the directionality of biomineralization processes[2]. In both cases, the application of the basic X-ray-diffraction (XRD) configuration with a $\theta/2\theta$ scan in the plane orthogonal to the sample normal results in a strongly biased spectrum due to the preferential alignment of the grains. For a fcc metal thin film such as gold, silver, platinum or copper, only the peaks corresponding to the typical (111) out-of-plane texture appear in the basic XRD spectrum. This hinders a reliable phase analysis, which is commonly achieved by comparing the XRD spectrum under investigation with a database of powder spectra. A trivial, but destructive way to obtain a XRD powder spectrum of a highly out-of-plane textured specimen is to crush the sample, e.g., as demonstrated for a *Meretrix lusoria* sea shell by Zhu *et al.*[2]. For weak and medium textured thin films, where a few peaks still appear but with inappropriate height ratios, some efforts have been reported in literature to correct the XRD intensities by measuring rocking curves of a few XRD peaks followed by some calculations[3],[4]. In the crystallography community it is common to use multiple Eulerian angle scans for the determination of the Orientation Distribution Functions (ODF) followed by the reconstruction of pole-figures, phases and residual stresses using neutrons or synchrotron X-rays[5, 6]. This technique is indeed very general and contains all required information, but the analysis of the data is highly complex and the set up of the experimental facilities (synchrotron-/neutron sources, beamline, detector systems) very expensive. Other researchers report successful phase analysis of heat-
resistant steels of the HP series by a combination of Electron BackScattered Diffraction (EBSD) and Energy Dispersive Spectroscopy (EDS), where EDS yields the composition and EBSD the corresponding crystallographic system[7]. Also this technique requires an intense analysis effort since especially the interpretation of the Kikuchi patterns of the EBSD measurements is usually highly complex. In the present paper, a simple variation of the basic XRD technique is proposed, where the powder-like spectra of highly textured specimens are obtained over a wide $\theta/2\theta$ angular range from a multi-axes scan using a common XRD source-detector setup together with an Eulerian cradle and automation software typical for commercially available XRD systems. The results of the proposed experiment do not contain the same amount of information as the complete multi-axial scans performed by the crystallographers, but this setup allows the use of commercially available and much less expensive equipment. Moreover, the output of this kind of measurement is immediately readable and requires a significant reduced amount of post-processing. We demonstrate for several of out-of-plane textured specimens such as Ti-Ni-Cu shape memory alloy thin films, Pt-W alloy thin films and sea shells that this relatively simple experiment can significantly improve the understanding of their properties such as (qualitative) phase composition, texture and residual stress. The robustness of this technique is demonstrated by showing results obtained with different diffractometers.
2.3 Experimental

The XRD intensity, I, of highly out-of-plane textured specimens is acquired as a function of the diffraction angle $2\theta$ (symmetric $\theta/2\theta$ diffraction geometry) and the Eulerian angle $\psi$ as illustrated in Figure 2.1.

![Figure 2.1: Scheme of the experimental setup: $\theta$ corresponds to the incident angle, $2\theta$ to the diffraction angle, $\psi$ to the Eulerian angle.](image)

The specimens are mounted on a standard X-ray diffractometer equipped with an Eulerian cradle and a beam size limiting pre-optical device (monocapillary, polycapillary). In practice, the XRD intensity $I(2\theta, \psi)$ is acquired for a discrete set of Eulerian angles $\psi_i$ where reasonable step sizes $\Delta \psi = \psi_{i+1} - \psi_i$ are in the range of 0.5°-1.5°. The angular range is chosen to obtain sufficient information with a maximum Eulerian angle $\psi_{\text{max}}$ of at least 60°. The measurement procedure can be easily implemented in the standard software of the diffractometer, e.g., for the PANalytical X'Pert Pro™ XRD
system (which was used for one of the samples) by means of a recursive algorithm, where a basic $\theta/2\theta$ XRD scan is followed by an incremental rotation $\Delta \psi$. This set of two instructions is repeated pre-defined number of times until the desired angular range has been spanned (a more detailed description of the recursive algorithm is given in the Appendix). For a metal film with a thickness ranging from 200 nm to 1000 nm, it is reasonable to expect a measurement time of 2 to 6 hours with this setup. The measurement time depends on the $2\theta - \psi$ angular measurement range and resolution, as well as on the signal to noise ratio and the source-detector technology. Finally, the data are visualized in a 2D plot by an appropriate program such as ORIGIN™, MAUD [8] or a custom made MatLab™ program. The XRD intensity is linearly dependent on the diffracting volume as a function of the diffracting angle $2\theta$ and the Eulerian angle $\psi$ which must be, to a first order, considered by

$$\tilde{I}(2\theta,\psi) = I(2\theta,\psi) \cdot f_g(2\theta,\psi) = I(2\theta,\psi) \cdot \sin \theta \cdot \cos \psi$$  

Equation 2.1

where $f_g$ is the geometrical correction factor, obtained by basic trigonometric considerations, and $\tilde{I}(2\theta,\psi)$ is the XRD intensity normalized by the diffracting volume. Single crystalline substrates such as silicon or sapphire, give additional peaks in the 2D plots and could lead to steady reflections if one of the main crystallographic axes of the wafer is aligned with the beam. The
latter effect can be reduced by rotating the substrate of a few degrees with respect to the surface normal.

2.4 Results

Figure 2.2 illustrates a typical result for the above described procedure for a *Haliotis rufescens* sea shell. This bulk material consists of oriented CaCO$_3$ platelets in an organic matrix. The sample was scanned in the range of $2\theta \in [20^\circ;120^\circ]$ and $\psi \in [0^\circ;70^\circ]$ with a step size of $\Delta\psi = 1^\circ$ using a standard PANalytical X’Pert Pro™ X-ray diffractometer equipped with a copper anode (Cu $K_\alpha$ radiation), a nickel filter, a 300 $\mu$m mono-capillary, an Eulerian cradle (which enables angular ranges of $\psi \in [0^\circ;85^\circ]$) and a position sensitive X-Celerator™ detector. With a basic symmetric XRD scan applied to this sample ($\psi = 0^\circ$), Fig. 2.2b, only the (002) out-of-plane texture component appears at the XRD spectrum while all remaining peaks referring to planes at an angle $\psi \neq 0^\circ$ with respect to the (002) texture disappear. The inactive planes for a basic XRD configuration become successively accessible by tilting the specimen by the Eulerian angle $\psi$ as shown in the 2D plot in Figure 2.2a. The total XRD measurement time for the *Haliotis rufescens* sea shell was approximately 5 h.
Fig. 2.2: XRD investigation of a Haliotis rufescens sea shell: a) multi-axes scan in the range of $2\theta \in [20^\circ;120^\circ]$ and $\psi \in [0^\circ;70^\circ]$, b) basic $\theta/2\theta$ XRD scan for $\psi = 0$ and c) powder-like XRD spectrum obtained by the projection of the corresponding multi-axes scan shown in (a) on the $I/2\theta$-plane. In a), the intensities are corrected using Equation 1. In b), only peaks according to the (002) out-of-plane texture appear while in c) also the remaining peaks appear. For clarity, some peaks have been indexed and the spectra in b) and c) are normalized to the peak of the (002) out-of-plane texture. The inset in a) shows a section of the (002) peak along the $2\theta$ direction which was used for the Scherrer analysis (cf. text).
This multi-axes scan can be also applied to metal thin films as shown in Figure 2.3a for a magnetron sputter-deposited Pt-W alloy thin film with a thickness of 500 nm on a silicon substrate. The measurement was carried out in the range of \(2\theta \in [20^\circ;90^\circ]\) and \(\psi \in [0^\circ;85^\circ]\) \((\Delta \psi = 1^\circ)\) using a BRUKER D5000 diffractometer, which is equipped with a Cu rotating anode, an 260° Eulerian circle, a point detector, and a 300 \(\mu\)m x 300 \(\mu\)m poly-capillary. All peaks appearing in the 2D plot can be attributed to Pt and no peaks according to W appear. The peaks which appear at \(\psi=0^\circ\) at about \(2\theta=40^\circ\), \(2\theta=86.4^\circ\) and \(2\theta=69.3^\circ\) originate from the Pt (111) and (222) planes and from the silicon substrate. Consequently, the W is present in solid solution in the (111) out-of-plane oriented Pt matrix. Another application of this technique is related to combinatorial studies. In these experiments, samples are produced so to have the variation of one or more parameters (e.g., thickness or composition) in a direction parallel to their surface, allowing the exploration of one or more properties as a function of the position on the sample surface. An example of such application is reported in Figure 2.4a showing multi-axial scans of a magnetron sputtered Ti-Ni-Cu shape memory thin film with a thickness of 800 nm on a silicon substrate. This sample has been produced by means of simultaneous magnetron sputtering of the three elements (co-sputtering) with the aim of producing a compositional gradient parallel to the surface of the sample. After the deposition, the film was annealed at 1000 K and then quenched to room temperature.
Fig. 2.3: a) 2D multi-axes XRD plot of a Pt-W alloy thin film with a thickness of 500 nm on silicon substrate. All peaks can be attributed to a (111) out-of-plane oriented Pt matrix. Since no peaks originating from W appear in the 2D plot, the W atoms have to be in solid solution in the Pt Matrix. The inset in a) shows a section of the (311) peak at $\psi=58^\circ$ along the $\psi$ direction which was used for the analysis of the texture's width (cf. text). b) Lattice parameter $d$ of the Pt matrix, as calculated from the 20 positions of the XRD peaks, as a function of the corresponding $\sin^2\psi$ value. From the slope of the linear fit, an equibiaxial residual stress of $+660\pm70$ MPa is calculated.
The variation in phase composition and texture along the surface of this sample are explored by using a series of multi-axial scans in the range of $2\theta \in [20^\circ;100^\circ]$ and $\psi \in [0^\circ;85^\circ]$ placed in the positions represented by a 6x6 mesh with lateral distances of 8 mm in both directions. The center of the measuring grid is congruent with the center of the wafer. For this measurement, the sample was mounted on a PANalyical X'Pert MRD™ system with a Cu source, an X-ray lens with a spot size of 500 μm, a position sensitive X-Celerator™ detector and a full circle Eulerian cradle with an x/y stage. To reduce the steady deflection of the single crystalline Si substrate, the sample was tilted by 15° around the surface normal. For clarity (and also due to constraints in place for figures), only a connected sub-region of a 3x3 grid (fourth quadrant of the overall grid) is shown in Figure 2.4a. The 2D plots evidence changes in peak position along the $2\theta$ direction as well as in $\psi$ direction which indicate changes in phase and texture. Some peaks are superimposed by a homogenous line along the $\psi$ direction which indicates an isotropic fraction of the specimen.
Fig. 2.4: a) 2D multi-axes XRD plots of an inhomogeneous Ti-Ni-Cu shape memory alloy thin film of 800 nm thickness on Si substrate and b) the corresponding powder-like spectra. The 3x3 measuring grid had lateral distances of 8 mm. The corresponding composition of the measuring points is given in b) for the vertices of the measuring grid. In good approximation, the gradients in between can be considered linear. It becomes evident, that the phases and texture strongly depends on the composition.
2.5 Discussion

Multi-axes scans contain information about phase composition, texture, grain size and residual stress of the specimen which will be discussed in detail in the following. Even a qualitative phase analysis of out-of-plane textured specimens using the basic \( \theta/2\theta \) XRD configuration is nearly impossible since: 

\( i) \) only peaks corresponding to the texture appear in the XRD signal and 
\( ii) \) both the texture and the phase composition of the specimen influence the XRD spectrum. This is demonstrated in detail for the *Haliotis rufescens* sea shell, where for the basic XRD configuration (\( \psi = 0 \)), only few peaks corresponding to the (002) texture appear (Figure 2.2b). Summing the XRD intensities \( \tilde{I}(2\theta,\psi) \) of a multi-axes scan over all \( \psi \) angles yields

\[
\tilde{I}(2\theta) = \sum_{\psi} \tilde{I}(2\theta,\psi) \quad \text{Equation 2.2}
\]

This quantity also includes information about the peaks originating from planes which are not parallel to the surface and corresponds to a "subset" of the powder-like spectra of the specimen. For a full powder-like XRD spectrum, \( \psi \) should be scanned over the complete range of 0 - 90° which is not feasible since the projection of the X-ray beam on the specimen surface becomes infinite for \( \psi = 90^\circ \). Peaks which exclusively appear in the complementary range of \( \psi \in (\psi_{\text{max}},90^\circ) \) with respect to the out-of-plane texture
of the specimen are still missing in the powder-like XRD spectrum (which is unlikely for reasonable $\psi_{\text{max}}$ of 70° since e.g., in fcc materials, prominent angles between low indexed directions are $45^\circ$, 54.7° and 35.3° for the [100]/[110], [100]/[111] and [110]/[111] axes, respectively) and peaks which partially appear in the complementary range of $\psi \in (\psi_{\text{max}}, 90^\circ)$ are indeed present in the powder-like XRD spectrum but have inaccurate intensity. It is also important to note that, due to statistical reasons, the peaks originating from the out-of-plane texture component have an increased intensity compared to the other peaks. For a tilted out-of-plane texture as well as for possible in-plane textures, the intensities of the powder-like spectrum also depend on the in-plane orientation of the specimen with respect to the sample normal. Nevertheless, the powder-like spectrum of a textured specimen significantly eases a qualitative phase analysis since it enables the use of common powder-diffraction databases such as the Inorganic Crystal Structure Database (ICSD) of the FIZ Karlsruhe (Germany). For the *Haliotis rufescens* sea shell, numerous additional peaks appear in the powder-like spectrum (Figure 2.2c) which could be attributed to the peaks of the orthorhombic phase of CaCO$_3$ (Aragonite)[2, 9]. For a quantitative phase analysis, the XRD intensity must also be acquired as a function of the azimuthal angle $\phi$ which allows for both the calculation of the ODF (followed by a quantitative phase analysis by reconstruction of the pole-figures) and the projection of $I(2\theta, \psi, \phi)$ on the $I(2\theta)$-plane (extension of the sum in Equation 2 on the azimuthal angle $\phi$) which again corresponds to the
complete powder-like spectrum. However, these measurements are very time consuming taking up to several days per sample as mentioned by Lutterotti et al. [10]. The average dimension $d$ along the normal of the investigated plane can be estimated by the peak broadening of the corresponding XRD signal along the $2\theta$ direction, which is well known as Scherrer’s analysis, according to [11]

\[
\bar{d} = \frac{0.9 \lambda}{\omega_i \cdot \cos \theta_i} \quad \text{Equation 2.3}
\]

In this formula, $\bar{d}$ is the average size, $\lambda$ is the wavelength of the X-rays, $\omega_i$ is the full width of half maximum (FWHM) of the $i^{th}$ peak in radian measured and $\theta_i$ is the corresponding Bragg angle. E.g., for the X-rays with wavelength $\lambda = 1.541874 \, \text{Å} \ (\text{Cu } K\alpha)$ and $\omega_{b02} = 4.3 \cdot 10^{-3}, \ \theta_{b02} = 15.56^\circ$ ((002) out-of-plane texture peak of the *Haliotis rufescens* sea shell - cf. inset of Figure 2.2a) an average platelet thickness of approximately 33 nm is obtained, which strongly differs from the platelet thickness of approximately 450 nm as determined by Scanning Electron Microscopy. This discrepancy is due to several reasons: i) a reliable grain size analysis is only achievable for grain sizes of less than 200 nm[11], ii) the peak is additionally broadened by the source/detector setup which has to be considered by an effective peak width $\omega_{\text{eff}}$, and iii) perturbation of the lattice periodicity additionally contribute to the peak broadening. All these reasons lead to a strong underestimation of the ‘real’
size of the particle. On the other hand, Barthelat et al.[12] report asperities on the surface of cleaved *Haliotis rufescens* sea shells with thicknesses of 10-30 nm as well as sub grains in the range of 3-10 nm. Secondly, it is important to note, that sea shells are a natural material which can strongly differ among each other, even within the same species. The texture of a sample is given by the peak positions in its XRD 2D plot ($2\theta;\psi$). For the Pt-W alloy thin film, all $2\theta$ peak positions can be attributed to Pt, where the peak at $(40.04^\circ;0^\circ)$ indicates a (111) out-of-plane texture. This is consistent to the peak positions of the remaining peaks, e.g., the (311) peaks at $(81.7^\circ;30^\circ)$, $(81.7^\circ;59^\circ)$ and $(81.7^\circ;80^\circ)$, which have appropriate tilt angles $\psi$ with respect to the (111) out-of-plane texture. The width of the texture is given by the half width of half maximum (HWHM) of a section along the $\psi$ direction of an arbitrary peak which is well known as rocking scan[11]. Quantifying a section of the (311) peak of the Pt-W alloy thin film at $(81.7^\circ;59^\circ)$ along the $\psi$ direction yields a HWHM of 2.5° which corresponds to a sharp texture (cf. inset of Figure 2.3a). The equibiaxial residual stress of a sample can be calculated using the $\sin^2\psi$-technique[13] which will be again demonstrated for the Pt-W alloy thin film. Basically, the lattice spacing $d_{hkl}$ obtained by Bragg’s equation from the $2\theta$ peak position shows a linear relationship on the $\sin^2\psi$-values of the corresponding Eulerian angle $\psi$[13]. Isotropic specimens show scattering of planes $hkl$ for all Eulerian angles, while for textured specimens, diffraction occurs only for well defined Eulerian angles $\psi$, e.g., at $\psi=0^\circ$ and $\psi=70.5^\circ$ for the (111) and (222) planes for a (111) texture. This limited number of
measuring points for fixed planes $hkl$ reduces the accuracy of the experiment. In the present case, all available peaks out of a multi-axes scan are included. The lattice parameter $d$ is plotted as a function of the related $\sin^2\psi$-value, which is shown in Figure 2.3b. With the exception of the (111) peak at $\psi=71^\circ$ and the (311) peak at $\psi=80^\circ$, the lattice parameter $d$ shows, to a good approximation, a linear behavior with regard to the $\sin^2\psi$-values. The deviation of these two peaks from the common linear behavior is due to the low precision of the experimental setup at i) low diffraction angles $2\theta$ and high Eulerian angles $\psi$ (111 peak at $2\theta=40^\circ$ and $\psi=71^\circ$) and ii) for very high Eulerian angles ((311) peak at $\psi=80^\circ$). Neglecting these two peaks, the remaining peaks can be fitted well by

$$d(\sin^2\psi) = 3.90225 + 0.01763 \cdot \sin^2\psi = b + m \cdot \sin^2\psi \text{ (in Å).} \quad \text{Equation 2.4}$$

For a (111) textured cubic specimen, the equibiaxial residual stress is given by [13, 14]

$$\sigma_{\text{residual}} \approx \frac{(C'_{11} + C'_{12}) \cdot C'_{33} - 2C'_{13} \cdot m}{2C'_{13} + C'_{33}} \cdot \frac{m}{b} \quad \text{Equation 5}$$

where $C'_{ij}$ are the elastic constants in (111) direction and $m/b$ is the quotient of the slope and the $y$-axis intercept as determined by Equation 4 for the Pt-W alloy thin film (please notice, that there are some typos in the explicit formula
(6) of Bohm et al.[14]). For Pt at room temperature (300 K), $C^i_{ij}$ are given by $C^i_{11} = 373$ GPa, $C^i_{12} = 250$ GPa, $C^i_{13} = 239$ GPa and $C^i_{33} = 385$ GPa[14, 15] which results in a tensile residual stress of $+660\pm70$ MPa of the Pt-W alloy thin film. Notice, that a similar result would be obtained for considering only peak pairs of fixed planes $hkl$; e.g., the (222) peak pair at $\psi=0^\circ$ and $\psi=71^\circ$ or the (311) peaks at $\psi=30^\circ$ and $\psi=59^\circ$ which would show similar slopes resulting in similar residual stresses (Figure 2.3b). Using only single peak pairs from planes $hkl$ could also result in highly misleading interpretation of the residual stress, if one of the unsuitable measuring points is included. Finally, this would result in a negative slope and within compressive residual stresses (Figure 2.3b) for the discussed Pt-W thin film system. The position sensitive measurements on the Ti-Ni-Cu shape memory thin film can be considered as an extension of the position sensitive basic XRD scans reported by Long et al.[16]. The peaks of the powder-like spectra of this sample (Figure 2.4b) can be attributed to the martensitic (M) and austenitic (B2) phase of TiNi. Differences in phase composition, as indicated by variations in the peak aspect ratios, are caused by the composition gradients. This material is a highly complex system with several overlapping XRD peaks which hinders a quantification of the phase composition by this technique. Nevertheless, the qualitative mapping of the phases as a function of the elemental composition can be used to interpret the relationship between material composition with the properties of interest (e.g., nanohardness, elastic modulus, electrical resistivity).
2.6 Summary & Outlook

Multi-axes XRD scans along the $2\theta$-axis and the $\psi$-axis were performed on several out-of-plane textured specimens using commercial XRD lab systems in combination with an Eulerian cradle. The projection of the 2D plot on the $I(2\theta)$-plane gives the corresponding powder-like spectrum, which enables the use of common XRD powder spectra databases for phase identification. It was also demonstrated, that additional information such as residual stress, texture and an estimation of the average grain size can be obtained out of the same multi-axes scan. For inhomogeneous samples with gradients in composition, this technique was applied in a position sensitive mode. The advantages of this technique are i) the use of commercially XRD systems instead of synchrotron or neutron sources and their corresponding detector systems, ii) data processing by standard software packages such as ORIGIN™ or MatLab™ and iii) its robustness which was demonstrated by applying several different XRD systems. These relatively simple modifications of the basic $\theta$/2$\theta$-XRD geometry can significantly improve the understanding of the thin film properties.

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2.8 Appendix

A short description on the recursive algorithm is given, which was used to perform the multi-axis measurements. The description explicitly refers to the standard software package of the PANalytical XRD system which was used in the present study. First, Program 1 has to be set up which consists of a basic symmetric \( \theta/2\theta \) scan in the range of \( 2\theta_{\text{min}} \leq 2\theta \leq 2\theta_{\text{max}} \). Subsequently, Program 2 is defined which consists sequentially of \( i) \) setting the initial Eulerian angle \( \psi_{\text{min}} \), \( ii) \) the measurement of Program 1 and \( iii) \) an incremental increase of the Eulerian angle \( \Delta\psi \). Finally, items \( ii) \) and \( iii) \) in between Program 2 are cycled till \( \psi_{\text{max}} \) is reached.
2.9 References


3 A combinatorial study on the influence of Cu addition, film thickness and heat treatment on phase composition, texture and mechanical properties of Ti-Ni shape memory alloy thin films


3.1 Abstract

A series of amorphous Ti-Ni-Cu based thin films with compositional spread and different thicknesses was produced at room temperature using a magnetron sputtering device and crystallized by means of different heat treatments. Phase composition and crystallographic orientation of the films were characterized using a Multi-Axial X-Ray Diffraction approach and their mechanical properties were assessed using nanoindentation. The results show that the addition of Cu and thermal treatments can be used to significantly alter the phase composition, the texture and the microstructure of the films. Film thickness plays an important role in determining of the amount of martensitic phase at room temperature as well as the amount of Ti-rich and
Ni-rich phases. In particular a thickness threshold between 350 nm and 800 nm was shown to be critical for the triggering of the texture in the austenitic phase.

### 3.2 Introduction

Since their discovery in 1959 [1], Ti-Ni based alloys gathered increasing interest in the scientific community due to their unique set of properties, and therefore potential applications, originating from the thermally induced austenitic to martensitic phase transition. Being the most prominent of these properties the ability of recovering shape after a plastic deformation, this material was the first to be designated as “shape memory alloy” (SMA). Many factors concur in a complex way to the determination of the shape memory effect making it difficult to represent with a single and unified model all the aspects of the transformation behaviour. Elemental composition [2], texture [3], grain size [4-6], stress state [7-9], geometry, size, position and coherence of eventual precipitates [10] are only a few of the studied features involved in this phenomenon [11]. The confirmation of the persistence of the shape memory effect also in the micro- and in the nanometric size (thin film) [12-15] opened the possibility of producing micro- and nanometric devices employing vapour deposition techniques together with the established forming procedures employed in microelectronics such as photolithography or focused ion beam [16-20]. Nevertheless, a possible drawback in the use of
these alloys in extremely miniaturized technologies comes from the fact that the shape memory effect is suppressed when the grain size is smaller than 60 nm [4-6]. Thin films often display uncommon features in their microstructure and for this reason they are known to show a peculiar physical behaviour compared to the same material in bulk [21]. Due to this fact, an increasing effort has been put in the last years to improve the understanding of the thermomechanical properties of SMA thin films in function of their microstructure. Under this point of view, two of the most distinguished features influencing SMA thin film properties, namely crystallographic texture and size effects, are to date rather poorly studied. Although some detailed theoretical studies about texture effects on bulk SMA are reported [22, 23], only very limited experimental literature exists up to date to support those studies in the case of SMA thin films. Similarly, although many works have been published to date about size effects on mechanical properties of thin films only very few specific experimental studies are reported about the influence of size effects on the transformation features of SMA thin films [24, 25]. On the contrary, many studies had as an object the influence of the addition of one or more alloying elements on the thermomechanical properties of the original binary alloy in the form of thin film [26]. Among all the studies about elements added to the Ti-Ni binary system, a substantially higher interest has been shown about the addition of Cu, due to the reduction of the transformation hysteresis [26-28], a key parameter in the field of micro electromechanical actuators. Due to all these reasons, it is evident the
importance of understanding the crossed relationships between composition and microstructure in the Ti-Ni-Cu ternary alloy. With the aim of exploring the outcome of a range of production parameters on the nanometallurgy of the Ti-Ni-Cu system, we present a combinatorial study about the effects of elemental composition, film thickness and thermal history on crystallography and mechanical properties of magnetron sputtered thin films. The reduced grain size (20-40 nm) induced in the entire batch of samples by the chosen thermal treatment did not allow a direct quantification the shape memory properties of the films due to the mentioned suppression of this effect for grain sizes below 60 nm [4-6].

3.3 Experimental details

In the following of this report, we will refer to elemental composition, always in atomic %, as, e.g.: Ti45Ni50Cu5 and to compounds as, e.g.: Ti45Ni50Cu5.

3.3.1 Sample production

The thin film samples were produced in a combinatorial mode using a PVD Products [29] sputtering device equipped with three magnetron guns installed in a circular fashion below the substrate (sputter-up configuration). Two guns, holding the Ti and the Ni target respectively, are positioned at the extremes of a diameter while a third one, bearing the Cu target, stands at an angle of 60° with the Ni bearing one. The principal axis of each gun is tilted 35° off the
normal to the substrate holder and, additionally, the gun heads can be independently further tilted ($x^\circ$, off-axis tilt) to control the sputter rate geometry over the sample surface. In Fig. 3.1, a sketch of the whole set-up is shown.

The target-to-substrate distance is about 145 mm. The chamber allows the in-situ thermal annealing of the samples by an array of IR lamps. Moreover, the chamber has been equipped with a custom designed contact cooling device,
enabling the in-situ quenching of the samples after annealing. As a substrate, single crystal Si wafers, (100) oriented, 3” diameter, 380 μm thick with 10 nm SiO₂ plus 200 nm Si₃N₄ diffusion barrier were used. All samples were positioned in the sputtering sample holder with the (010) direction of the single crystal substrate parallel to the direction of Ti and Ni magnetrons (see Fig. 3.1). The sputtering parameters were optimized to obtain an atomic composition of Ti50Ni45Cu5 in the centre of the sample, a convenient range for the composition of the single components: Ti(35-55)Ni(40-60)Cu(3.5-9.5) and a reasonably homogeneous film thickness (± 5%) all over the sample. Further details about the deposition parameters are given in Table 3.1.

<table>
<thead>
<tr>
<th>Table 3.1, sputtering parameters:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base pressure:</strong></td>
</tr>
<tr>
<td><strong>Sputtering Pressure:</strong></td>
</tr>
<tr>
<td><strong>Sputtering Gas:</strong></td>
</tr>
<tr>
<td><strong>Sputtering temperature:</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Power (W)</th>
<th>Off-Axis Tilt*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>320</td>
<td>+10°</td>
</tr>
<tr>
<td>Ni</td>
<td>170</td>
<td>+10°</td>
</tr>
<tr>
<td>Cu</td>
<td>16</td>
<td>-15°</td>
</tr>
</tbody>
</table>

* Positive tilt towards the center of the chamber

Sputter rate and film thickness homogeneity were determined by measuring FIB cross sections of the films in different positions across the surface of the sample. After the sputter rate determination, the desired film thickness was achieved by timing the deposition process. To evaluate the role of film thickness on the properties of interest, samples of 3 different thicknesses
were produced (~350 nm, ~800 nm and ~1600 nm), keeping the sputtering parameters constant (except time, obviously) in order to achieve the same composition distribution for all the samples. With the aim of studying the influence of the crystallization treatment on the texture (being the as-sputtered films completely amorphous), all the samples but one (800 nm thick) were annealed in vacuum (always better than 70 μPa) for 600 s at 800 K; the non-annealed one was used to evaluate the properties of the as-sputtered film. After annealing, all heat treated samples were quenched. To investigate the validity of the quenching procedure, one sample (800 nm thick) was allowed to freely cool in vacuum (furnace cooling) after the annealing. A summary of sample denomination with respective thicknesses and applied heat treatment is reported in Table 3.2.

Table 3.2, sample thickness:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sputtering Time, min</th>
<th>Approximate Thickness, nm</th>
<th>Thermal Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>12</td>
<td>~350</td>
<td>Annealing + Quenching</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>~800</td>
<td>Annealing + Quenching</td>
</tr>
<tr>
<td>C</td>
<td>30</td>
<td>~800</td>
<td>Annealing + Furnace cooling</td>
</tr>
<tr>
<td>D</td>
<td>60</td>
<td>~1600</td>
<td>Annealing + Quenching</td>
</tr>
<tr>
<td>E</td>
<td>30</td>
<td>~800</td>
<td>None</td>
</tr>
</tbody>
</table>
3.3.2 Morphology characterization by Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM), Focused Ion Beam (FIB) and Transmission Electron Microscope (TEM)

The surface of the films was analyzed using AFM (WITec CRM 200) and FIB/SEM (dual beam Carl Zeiss NVision 40). While both the AFM and the SEM were used to image the surface roughness, the FIB/SEM was employed to cut trenches in the films to determine the film thickness and grain morphology and to cut out TEM lamellae from spots where a detailed characterization was necessary. Cross-sectional TEM lamellae were prepared by milling the films perpendicularly to the substrate surface using a Ga-ion beam at 30 kV accelerating voltage. In the initial steps, 5 μm x 20 μm lamellae were thinned to approximately 1 μm thickness. The lamellae were then cut out of the substrate and transferred to a Cu TEM grid by using a micromanipulator installed inside the FIB chamber. In the final stages, the lamellae were thinned using beam currents progressively decreasing from 40 pA to 10 pA and reduced to final thicknesses of 100 nm to 200 nm which was enough to obtain electron transparency.

A transmission electron microscope Philips CM30 working at 300 kV was used in this work for microstructure characterization. A vapour-deposited gold reference powder sample was used for calibration of the microscope’s camera length.
3.3.3 Crystallographic characterization

Multi-Axial X-Ray Diffraction (MAXRD) [30] was used to study phase composition and texture of the films using a PANalytical X'Pert Pro™ XRD system equipped with a PIXcel™ line detector, a MRD™ Euler cradle and poly-capillary X-ray lenses with 1 mm diameter. The use of X-Ray focusing optics allows the measurement of spots with a diameter of about 2 mm (slightly varying with the source to substrate angle) over a 6x6 square grid of 40 mm side. It is worth to note that, to avoid an unreasonable duration of the measurement, the measurement parameters (exposure time and angular resolution) were adjusted to achieve a maximum measuring time per spot of around 2 hours and therefore a total measuring time per sample of 72 hours. With this aim in mind, the angular ranges were chosen to include the main reflections of the phases deemed to be possibly present in the films (TiNi, Ti2Ni, TiNi3, Ti3Ni4) and a reasonable amount of off-plane texture components, in particular: 38°<2θ<50° and -5°<ψ<65°. During the preliminary measurement set-up it was found that the measurements were affected by heavy artefacts in the form of straight lines of high diffracted intensity at fixed ψ angles. The cause was determined in the nature of the substrate, which, being a single crystal, was generating steady reflections at definite ψ angles if aligned with the diffractometer main axes. To avoid these reflections it was chosen to impose to the measurement grid a slight offset in the φ angle with the main crystallographic directions of the substrate. This angular offset led to a misalignment between the positions of the XRD
mappings and the nanoindentation mappings, which were performed in a previous moment on all same samples. Interesting features that can be distinguished in the “orientation plot” (Fig. 3.2a, 3.3a, 3.4a and 3.5a) are the distribution of the crystallographic orientation of the grains and for every phase, while the “powder like plot” (Fig. 3.2b, 3.3b, 3.4b and 3.5b), derived from the “orientation plot” by integrating the intensity along the $\psi$ direction, can be used to estimate the relative phase composition and in general to compare the data collected in the thin films with the existing databases for powder diffraction spectra. The ternary projections of the mechanical properties (discussed in the following of this report) shown Fig. 3.6a-h can be used to have an indication of the elemental composition of every subplot, whose position in the compositional space is marked with an inset reporting its row and column number. In the “orientation plot”, the signal intensity is plotted as a grey-scale range and it is normalized to the maximum intensity in every sub-plot, while in the “powder like plot” the sub-plots are presented with a common y-axis scale range, normalized to the maximum count reading among all the sub-plots of the same sample. The position sensitive plots will be discussed individually for each sample, following the denomination given in Table 3.2.
Fig. 3.2 Sample A: 350 nm, annealed and quenched, MAXRD, a: “orientation” plot, b: “powder-like” plot. The inserts are an example of the denomination of the subplots (Row-Column) in Fig. 6a-h. Symbols used: T = Ti$_2$Ni; A = TiNi B2; R = TiNi-R; O = TiNi-B19; M = TiNi-B19'; N = Ti$_3$Ni$_4$. 
Fig. 3.3 Sample B: 800 nm, annealed and quenched, MAXRD. a: “orientation” plot, b: “powder-like” plot. The position of the TEM lamellae L1 and L2 (see Fig. 10-11) is shown in the circles. Symbols used: T = Ti2Ni; A = TiNi B2; R = TiNi-R; O = TiNi-B19; M = TiNi-B19'; N = Ti3Ni4; W = TiNi3
Fig. 3.4 Sample C: 800 nm, annealed and furnace cooled, MAXRD, a: “orientation” plot, b: “powder-like” plot. The position of the TEM lamella L3 (see Fig. 12) is shown in the circle. Symbols used: T = Ti2Ni; A = TiNi B2; R = TiNi-R; O = TiNi-B19; M = TiNi-B19'; N = Ti3Ni4; W = TiNi3.
Fig. 3.5 Sample D: 1600 nm, annealed and quenched, MAXRD, a: "orientation" plot, b: "powder-like" plot. Symbols used: T = Ti2Ni; A = TiNi B2; R = TiNi-R; O = TiNi-B19; M = TiNi-B19'; N = Ti3Ni4; W = TiNi3.
3.3.4 Mechanical characterization by nanoindentation

Nanoindentation measurements were performed using a TriboIndenter (Hysitron Inc, USA) with a Berkovich tip in displacement-control mode (100 nm maximum depth, loading/unloading rate 5 nm/s, 1 s holding time at maximum depth) over a 9x9 square grid (40 mm x 40 mm side) centred on the sample, with 5 repetitions for every indenting spot. The reported results are the average of the 5 measurement repetitions. The unloading segments of the curves were analyzed by the Oliver-Pharr method [31].
Fig. 3.6a Sample E: 800 nm, as sputtered, nanoindentation vs composition map for Reduced Young's Modulus.

Fig. 3.6b Sample E: 800 nm, as sputtered, nanoindentation vs composition map for Hardness.
Fig. 3.6c Sample B: 800 nm, as annealed and quenched, nanoindentation vs composition map for Reduced Young's Modulus. Insets indicate the positions of the related MAXRD scans (Row and Column number) reported in Fig. 3.3a-b.

Fig. 3.6d Sample B: 800 nm, as annealed and quenched, nanoindentation vs composition map for Hardness. Insets indicate the positions of the related MAXRD scans (Row and Column number) reported in Fig. 3.3a-b.
Fig. 3.6e Sample C: 800 nm, as annealed and furnace cooled, nanoindentation vs composition map for Reduced Young's Modulus. Insets indicate the positions of the related MAXRD scans (Row and Column number) reported in Fig. 3.4a-b.

Fig. 3.6f Sample C: 800 nm, as annealed and furnace cooled, nanoindentation vs composition map for Hardness. Insets indicate the positions of the related MAXRD scans (Row and Column number) reported in Fig. 3.4a-b.
Fig. 3.6g Sample D: 1600 nm, as annealed and quenched, nanoindentation vs composition map for Reduced Young's Modulus. Insets indicate the positions of the related MAXRD scans (Row and Column number) reported in Fig. 3.5a-b.

Fig. 3.6h Sample D: 1600 nm, as annealed and quenched, nanoindentation vs composition map for Hardness. Insets indicate the positions of the related MAXRD scans (Row and Column number) reported in Fig. 3.5a-b.
3.3.5 Elemental composition mapping by Energy-Dispersive X-ray Spectroscopy (EDX)

EDX maps of the samples were performed using a CAMSCAN SEM Series 4 equipped with a Baker Hughes Noran Instruments EDX detector. The EDX measurements were carried out at an acceleration voltage of 20 kV and an acquisition time of 60 s over a 6 x 6 matrix of 1 mm x 1 mm spots covering a 40 mm x 40 mm area centered on the sample. Two samples were probed, (B and D) one with the EDX measurement matrix aligned with the nanoindentation measurement matrixes, and one with the EDX measurement matrix aligned with the MAXRD scan matrixes. This double measurement was required both for providing compositional coordinates for the nanoindentation and for the MAXRD data, whose grids are misaligned of 15°, and also to verify the reproducibility of the compositional distribution among the samples.
3.4 Results

3.4.1 FIB, SEM and AFM characterization

A typical FIB/SEM image of an annealed film (Sample B) is shown in Fig. 3.7. In the top view, Fig. 3.7a, the surface appears composed of structures each one having a diameter of around 10-15 nm organized in clusters of 25 to 40 units with a total diameter around 30-60 nm with cracks running between the clusters. The FIB sections of the films shown in Fig. 3.7b and the side view of a cracked film in Fig. 3.7c suggest that the clusters extend in depth in a columnar fashion, as also reported in literature for films produced in similar conditions [8].

Fig. 3.7 SEM scans of Sample B: a. Top view of grain structure with intergranular cracks; b. FIB cross-section view; c. Detail of columnar grains.

In Fig. 3.8 typical AFM scans of the film surface before and after crystallization are reported. The most evident feature of the crystallized film (Fig. 3.8b) compared to the as-sputtered one (Fig. 3.8a) is the different size and distribution of the cracks, which seem to coalesce in the heat treated
sample while the smaller structures observed in the SEM images seem to exist already in the as-sputtered samples.

![AFM scans of film surface](image)

Fig. 3.8 Typical AFM scans of the film surface before (a) and after (b) crystallization. In both samples, peak-to-valley maximum height is around 7.5 nm.

The roughness analysis carried out on the AFM scans report values of 2.4 nm root mean square (RMS) for the as-sputtered sample and of around 3.0 nm RMS for the crystallized ones.

### 3.4.2 EDX mapping

Since all samples were produced under the same conditions and using the same sputtering parameters, the distribution of the elemental composition on their surface was not expected to vary significantly from sample to sample. To prove this assumption, two samples were mapped and compared, confirming the reproducibility of the compositional spread. Fig. 3.9 shows the results of the EDX elemental composition mapping of a 40 mm side square area centred on sample D, visualized as level plots.
Fig. 3.9 EDX Mapping of Sample D. In the plots, level lines interpolated from the discrete data points are shown. The measurement grid has been rotated of 15° compared to the (100) crystallographic direction of the sample (see Fig. 3.1) to make it parallel to the MAXRD measurement grid (Fig. 3.2-3.5). The i-j axes in the first plot show the crystallographic orientation (100) of the single crystal Si substrate. The crosses mark the positions where the EDX measurements were performed.

A system of axes (i-j) parallel to the (100) crystallographic orientation of the single crystal Si substrate is also shown in the first plot. As can be seen in the diagrams, due to the asymmetrical configuration of the magnetrons in the sputtering facility, the elemental composition distribution forms different angles with the X and Y axes of the measuring grid. In particular, the Ti and Ni isocompositional lines are almost parallel to the X axis while the Cu isocompositional lines are angled compatibly with the geometric disposition of the Cu target.
3.4.3 MAXRD

Table 3.3 resumes all the phases observed among the analysed samples including the data used to interpret the diffraction spectra in the following of the paper [32-37].

Table 3.3, Phases observed within all the samples

<table>
<thead>
<tr>
<th>Chemical Formula (Phase Name)</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Lattice parameters</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td>TiNi (Austenite)</td>
<td>Cubic B2</td>
<td>Pm-3m</td>
<td>2.998</td>
<td>2.998</td>
</tr>
<tr>
<td>TiNi (Martensite)</td>
<td>Orthorhombic B19</td>
<td>Pnmb</td>
<td>2.919</td>
<td>4.288</td>
</tr>
<tr>
<td>TiNi (Martensite)</td>
<td>Monoclinic B19'</td>
<td>P21/m</td>
<td>2.884</td>
<td>4.11</td>
</tr>
<tr>
<td>Ti2Ni</td>
<td>Cubic Fd-3m</td>
<td>11.319</td>
<td>11.319</td>
<td>11.319</td>
</tr>
<tr>
<td>TiNi3</td>
<td>Hexagonal P63/mmc</td>
<td>5.093</td>
<td>5.093</td>
<td>8.32</td>
</tr>
<tr>
<td>Ti2Ni4</td>
<td>Rhombohedral R-3</td>
<td>11.235</td>
<td>11.235</td>
<td>5.0789</td>
</tr>
</tbody>
</table>

3.4.3.1 Sample A, 350 nm, annealed and quenched

The constant counts at all the $\psi$ tilts, appearing as vertical “stripes” in the orientation plot related to all the measurement positions on the sample A, Fig. 3.2a, show that only randomly oriented crystallites are present all over the sample. Nevertheless, the powder-like plot, Fig. 3.2b, reveals a strong variation in the phase composition, with homologous regions that appear almost parallel to the Ni iso-compositional lines. In particular, a significant fraction of the intermetallic phase Ti$_2$Ni appears in the upper 2/3 of the explored region in the sample, corresponding to a composition included in
Ti(>52)Ni(<41)Cu(4-7). In the same interval of composition, weak peaks from TiNi austenitic phase (cubic B2) can be identified and always associated with the pre-martensitic R-phase (rhombohedral). The intensity of the R-phase peaks increase in the range Ni(41-50), proportionally to Ni content, until the complete transformation of this phase to TiNi martensite (a mixture of orthorhombic B19 and monoclinic B19'), Ni(>50). In the lower part of the sample it is also possible to recognize some weak peaks belonging to the intermetallic phase Ti₃Ni₄. In the central region of the sample the contemporary presence of many phases makes it difficult to clearly define the Austenite-Martensite transition, due to the fact that the main peaks of these two phases are very close in the $2\theta$ range. Nevertheless, it is possible to roughly estimate the composition having the martensitic transition at room temperature (M$_{sRT}$) (in cooling from the heat treatment) around Ti(45-50)Ni46.5Cu(3.5-8.5).

### 3.4.3.2 Sample B, 800 nm, annealed and quenched

This sample, shares with the previous all the production parameters except the thickness, and therefore it is equivalent under the point of view of the elemental composition distribution. Nevertheless, it is remarkably different than the latter concerning both phase composition and crystallographic orientation. The first and most distinguished feature appearing in the orientation plot, Fig. 3.3a, is the presence of a region, with approximate elemental composition of Ti(<52)Ni(<44)Cu(4-7), where a marked texture of
the TiNi phase (Austenite and R-phase) is recognizable. In this region, the
dominant phase is a (110) textured TiNi austenite mixed with an isotropically
oriented Ti$_2$Ni towards the increasing Ti and with a partially textured R-phase
and with an isotropic martensite towards the Ni rich region of the sample, as
shown in Fig. 3.3b. The maximum signal intensity related to the B2 phase
appears around an elemental composition around Ti$_{53}$Ni$_{41}$Cu$_6$. As in the
case of the previous sample, it is possible to recognize regions “parallel” to
the Ti-Ni gradient which have similar phase compositions. In the regions with
Ni(>46) a significant amount of martensite, with a maximum around
Ti$_{42}$Ni$_{51}$Cu$_7$ can be identified. In the Ni-rich side of the sample it is possible
to recognize the contemporary presence of monoclinic (B19') and
orthorhombic martensite (B19). Like for the previous sample, the $M_{sRT}$
composition can be estimated around Ti$(45-50)$Ni$_{46.5}$Cu$(3.5-8.5)$, see Fig.
3.6c-d. Finally, as for the previous sample, the Ni(>53) region of Sample B
shows a dominating martensite phase with some weak peaks belonging to
the phase Ti$_3$Ni$_4$.

3.4.3.3 Sample C, 800 nm, annealed and furnace cooled

In Sample C, the lower half of the orientation plot, Fig. 3.4a, in the region with
Ni(>46), looks quite similar to the one of the quenched sample regarding both
phase composition and texture, with no specific preferential orientation for
any of the phases recognizable in the powder-like plot, Fig. 3.4b. The upper
portion of the orientation plot, instead, suggests both a change in texture from (110) in the quenched film to (100) in the furnace cooled one and a gradual distortion of the original B2 phase to at least two forms of pre-martensite phases. The (faint) austenite peak in the plot situated in Fig. 3.4a, row n.2, column n.6, is clearly seen to split first in two and then in four peaks moving towards the columns on the left of the array of plots, when the concentration changes from Ti56Ni40Cu4 to Ti52Ni41Cu7. This peak splitting is evidenced in the plot by superimposed black arrows. In particular, the main directions and the amount of the lattice distortion in function of the Cu content can be inferred by fitting the position of the peaks originated from the splitting of the original austenitic one. Fitting the peaks in the sequence of subplots in Fig. 3.4a, row n.2 starting from column n.6 to column n.1, it can be noticed how the single TiNi austenite peak positioned around $2\theta = 42.45^\circ$ and $\psi = 45^\circ$ gradually splits first in two peaks having the same $2\theta$ direction of the original peak and symmetrically positioned around $\psi = 45^\circ$, then into four peaks. Table 3.4 shows the results of the fitting of the peak positions in $2\theta$ and $\psi$ in function of the elemental composition. The $M_{sRT}$ composition can be estimated around Ti(45-50)Ni46.5Cu(3.5-8.5), see Fig. 3.6e-f.
3.4.3.4 Sample D, 1600 nm, annealed and quenched

Sample D (Fig. 3.5a), the thickest in the set, shows a partially textured TiNi austenitic phase mixed with significant amounts of isotropic Ti$_2$Ni in the composition range Ti(48-56)Ni(40-45)Cu(4-7), with a maximum value for the TiNi austenite peak around Ti$_{55}$Ni$_{41}$Cu$_4$. In the rest of the sample, the XRD orientation plots show only isotropically oriented TiNi martensite mixed with TiNi$_3$ and Ti$_3$Ni$_4$ intermetallic phases. The comparison of this sample with Samples A and B, same heat treatment but different thicknesses, shows some important differences. Compared to the thinner Sample A, Sample D reveals i) a higher fraction of austenitic phase, and therefore less Ti$_2$Ni, in the Ti rich side of the mapped area, and ii) the presence of peaks associated with TiNi$_3$, which was not clearly evidenced in any of the thinner samples. Moreover, XRD martensite patterns in Sample D around a composition of Ti$_{42}$Ni$_{50}$Cu$_8$ show a strong signal coming from (±111) peaks around $2\theta = 41.3^\circ$ and $2\theta = 45^\circ$, not like Samples A and B where only the (020) peak
around \( \theta = 44^\circ \) is visible. As for the previous sample, the \( M_{sRT} \) composition can be estimated around Ti(42.5-47)Ni49(4-8.5), see Fig. 3.6g-h.

### 3.4.3.5 Sample E, 800 nm, as sputtered

Sample E, as-sputtered and without any heat treatment, as expected for a room temperature deposited SMA film, shows the classical broad peak referred to completely amorphous materials, without any noticeable difference among all the scanned regions in the sample.

### 3.4.4 TEM characterization

To confirm the results of the MAXRD and characterize the microstructure of the films, three lamellae were cut out by FIB and investigated by TEM. Two of them, denominated L1 and L2, were cut from two regions of sample B, precisely from a highly textured TiNi austenitic spot and from a spot deemed to contain a mixture of isotropically oriented TiNi martensite and Ni\(_3\)Ti intermetallic phase, (Fig. 3.3a-b, Fig. 3.6c-d). The last one, L3, was cut from a region of sample C, (Fig. 3.4a-b, Fig. 3.6e-f), where MAXRD indicated the presence of an isotropically oriented TiNi martensite with a significantly different x-ray diffraction fingerprint compared to the region where L2 was cut from.
3.4.4.1 Lamella L1

Fig. 3.10 shows transmission electron images of the lamella L1 (Sample B, Ti53Ni 41.2Cu 5.8).

Fig. 3.10 TEM images of selected spot on Sample B (see Fig. 3.3a-b, 3.6c-d, L1 lamella). In bright field images 'a' and 'b' the columnar grain structure of the film is visible. Image C shows the selected area electron diffraction pattern from the region marked in 'a', confirming that groups of grains share nearly the same crystallographic orientation. Image 'd' shows a dark field image recorded using the [110]-type reflection marked in the inset, revealing that not all grains span the entire film thickness.

The film has a thickness of 830 nm. Bright field micrographs (Figs. 3.10a-b) show a microstructure made of columnar grains of width 20 to 40 nm, Fig. 3.10c shows the diffraction pattern recorded along the (111) crystal direction of the TiNi austenite from the area marked with a circle in Fig. 3.10a. This area, like others in the sample, contains several grains. However its diffraction pattern looks single-crystal-like. This indicates that several grains
are grouped together with almost the same orientation. The film presents a texture with grains of the B2 phase oriented with the (110) direction perpendicular to the substrate. The dark-field image in Fig. 3.10d indicates that some grains do not extend through the whole film thickness.

3.4.4.2 Lamella L2

Figs. 3.11a-b show bright-field electron images of the lamella L2 (Sample B, Ti 42Ni51.3Cu6.7).

Fig. 3.11 TEM images of selected spot on Sample B (see Fig. 3.3a-b, 3.6c-d, L2 lamella). Images ‘a’ and ‘b’ show a bright field view where only randomly oriented grains are visible. Image C shows the selected area electron diffraction pattern from the region marked in ‘a’. Image ‘d’ shows a dark field view of the lamella from the reflections marked in the inset.
The film has a thickness of 740 nm and appears polycrystalline. The
diffraction pattern of Fig. 3.11c confirms that the grains are randomly
oriented. From the dark-field electron image (Fig. 3.11d), obtained by using
several reflections from the brightest diffraction rings, it is possible to estimate
the grain size, which ranges from 10 to 50 nm.

3.4.4.3 Lamella L3

Fig. 3.12a shows a bright field images of the lamella L3 (Sample C, Ti
41Ni54.5Cu4.5).

Fig. 3.12 TEM images of selected spot on Sample C (see Fig. 3.4a-b, 3.6e-f, L3 lamella).
Images ‘a’ and ‘b’ show a bright field view of the lamella, evidencing martensitic grains. In
image ‘d’ a detail of the twinned structure of a martensitic grain is shown. Image ‘c’ shows the
electron diffraction pattern from the area marked in ‘a’.
The top film surface has been partially eroded by the FIB milling process, therefore a determination of the original thickness was not possible. The diffraction pattern shown in Fig. 3.12c confirms that the film is polycrystalline and grains are randomly oriented. The bright field images (Fig 3.12b and 3.12d) display a few elongated grains of the martensite phase B19' which are identified by their typical twinned structure.

### 3.4.5 Nanoindentation

The mechanical properties of samples B, C, D and E were characterized using nanoindentation. To show the correlation of the mechanical properties in terms of elemental composition, it has been chosen to represent the mapping of the mechanical properties as a projection on the ternary diagram Ti-Ni-Cu, Figs. 3.6a-h. Nevertheless, due to the limited extension of the explored region in terms of ternary coordinates, with the aim of facilitating the visualization of the results, every figure is shown as a magnification of the ternary diagram in the range: Ti(35-61)Ni(30-62)Cu(3-10). Moreover, to correlate the information coming from the crystallographic analysis to the mechanical characterization, in every plot (except for Sample E for which no MAXRD has been reported) the position of the MAXRD scans is represented with a square carrying the coordinates in terms of row and column of the corresponding subplot of Figs. 3.2-3.5. Significant variations in hardness and Young’s moduli were found within the measured area in every sample and among the average hardnesses of all the samples. The extreme values for $H$
ranged from 3.8 GPa in the as-sputtered sample (amorphous) and up to 7.5 GPa in the Ni rich regions of furnace cooled, 800 nm thick Sample C. The lowest values for the elastic modulus $E_r$ were measured in the Ni rich regions of the 1600 nm thick Sample D, 100 GPa, and the highest in the Ti rich regions of Sample C, 154.5 GPa.

3.5 Discussion

The results coming from the position sensitive MAXRD analysis suggest a complex interaction between elemental composition and crystallization mechanisms within each film. Both the “orientation plot” (intensity vs $2\theta$ and $\psi$) and the “powder like plot” (intensity vs $2\theta$) in all the samples show distinct and circumscribed areas of existence of several phases within the characterized area, and specifically TiNi B2 (austenite), TiNi R-phase (pre-martensite), TiNi B19 and B19’ (orthorhombic and monoclinic martensite), Ti$_2$Ni, Ti$_3$Ni$_4$ and TiNi$_3$. The comparison of the phase composition and microstructure among the films evidenced how film regions with equivalent elemental composition but different production parameters (thickness and heat treatment) show clear differences in the phase composition, microstructure, crystallography and mechanical properties. In particular, it has been demonstrated that film thickness and cooling rate are crucial in defining phase composition and texture of the crystallized films, and therefore their mechanical properties. A much reduced variability in the mechanical
properties in function of elemental composition was observed in amorphous films.

3.5.1 Phase composition and texture

3.5.1.1 The effect of elemental composition and Cu content

It is possible to identify some similarities, among all the crystallized samples, regarding phase composition in relation with elemental composition. In all the films, the TiNi austenite seems to be prevalent in the Ti rich regions with highest peak intensity always found close to values of Ti(52-54)Ni(39-42)Cu(5-7). This elemental composition range also coincides with the highest texture appearing in samples B and C. TiNi martensite appears prevalently above Ni(>47.5) and until the lower end of the composition range explored by MAXRD Ti(38-41)Ni(55)Cu(4-7). Moreover, the elemental composition of the regions where the transition between TiNi austenite and martensite occurs (on cooling from the crystallization process) is compatible with the values found in literature [2]. The analysis of the MAXRD scans in the martensite-rich regions of all the samples evidenced that the addition of Cu has an effect in changing the relative intensity \( I \) between the martensite peaks related to the (020) planes \( (2\theta \sim 44^\circ) \) and the peaks related either to the (1-11) or (111) planes \( (2\theta \sim 41.3^\circ \) and \( 2\theta \sim 44.9^\circ \) respectively) so that the ratio \( I_{(020)}/I_{(1\pm11)} \) builds up with the increasing in Cu content of the alloy. The orientation plot
showing no particular orientation discards the possibility of this finding to be the result of a texture effect. We believe that the explanation to this phenomenon could be related to the distortion of the original equiatomic TiNi alloy crystal lattice generated by the partial substitution of Ti and Ni atoms with Cu in the TiNi lattice causing a series of monoclinic/orthorombic martensite variants [33, 38-41]. Another explanation could come from the fact that the preferential twinning direction during the transformation of austenite to martensite may result in precipitates in plate or needle like fashion, so that the ratio among the peaks in XRD diffraction could change by the attenuation of one or more reflections. The presence of intermetallic phases other than TiNi is maximized outside of the interval Ti(43-56)Ni(40-50)Cu(4-8) and it is remarkable that, unlike the TiNi phase (austenite or martensite), neither Ti-rich nor Ni-rich intermetallic phases ever showed any sign of texture. The R-phase, when present, is partially textured, as expected, since this phase results from the distortion of the original cubic lattice of austenite. As the R-phase is the result of a deformation of the austenitic cubic lattice (cubic to rhombohedral), a splitting of the austenite diffraction peaks (maintaining the original texture) is also expected, at least at the beginning of the transformation. It is interesting to observe the evolution of the austenite peak with increasing Cu content in Sample C (Fig. 3.4a). This evolution, corresponding to a change in texture, is consistent with a sequence of lattice distortions (pre-martensite) of the original cubic phase (B2 austenite). The explanation we propose for the double splitting of the (110) peak belonging to
austenite is the following: i) due to the shifting of the martensitic transformation temperature of the alloy caused by the progressive substitution of some of the original atoms in the original Ti-Ni cubic cell by Cu, the original cell experiences first a cubic-to-rhombohedral distortion, with a shear of the (101) planes in the [-111] direction (considering the (100) as the out of film plane direction); ii) a compression of the (101) planes in the [101] direction (rhombohedral-to-monoclinic transformation). The mentioned transformations account for the described peak splits in the following way: the cubic-rhombohedral distortion maintains the distance between the (110) planes as in the original cubic phase and therefore does not produce a significant shift of the peaks in the $2\theta$ axis, but results in a split of the angle between the original cubic (101)/(-101) and (011)/(0-11) planes from $\psi = 45^\circ$ to $\psi = 45^\circ \pm \delta$ where $\delta$ increases with the amount of shear applied. The rhombohedral-to-monoclinic compression of the cell produces a change of such distance on only one couple of such planes, producing a splitting of the two existing peaks into four, parallel to the $2\theta$ axis.

### 3.5.1.2 The effect of film thickness

The total thickness of the starting amorphous film appears to be one among the parameters with the strongest influence on the final phase composition, grain size and texture of the crystallized samples. Phase composition and microstructure of sputtered films are known to be controlled by the effects of the interplay between interface energy and strain energy density [42, 43]. The
amounts of phases which are energetically favoured by interface effects (heterogeneous nucleation and interface energy) are expected to increase in films with increased surface-to-volume ratio (thinner) while the phases who minimize the strain energy density will be prevalent in thicker films. In literature, films with a similar elemental composition and sputtered at similar pressures have been found to exhibit high residual stresses [8]. The fact that no texture was found in the austenitic regions of the thinner samples can be explained by two concurring factors: first, the work published by Wang et al. [16, 43] where a strong dependence of grain growth rate on thickness has been evidenced and, second, again the well known strain vs surface/interface energy minimization criterion for texture selective grain growth in thin films [44, 45]. In our case, a much slower grain growth of equiatomic TiNi crystallites in thinner films may have led to a distribution of isotropically oriented small sub-grains rather than the (quasi-)single crystalline grains suggested by the sharper texture observed in the samples of middle thickness (800 nm). In this last case, a faster growth rate, together with an increased in-plane stress could have resulted in a much stronger selection of textured grains. The finding of (110) or (100) textured TiNi austenite in samples with the same thickness but different cooling rate could be ascribed to a relaxation of the stresses during the high temperature stay which may have caused the switching from strain energy driven to interface energy driven growth mode of the textured columnar grains. The TiNi austenitic phase, which in Sample B is dominant only in the Ti rich part of the explored
region and markedly textured, shows a more extended field of existence in the thicker Sample D, even down to Ni(<49). Moreover in Sample D, the TiNi austenite peak appears shifted to lower $2\theta$ angles, suggesting a lattice distortion maybe caused by residual stresses or by a slight deviation from the Ti-Ni 1:1 composition of the original cell. Comparing the peak intensity ratio between Ti$_2$Ni and TiNi austenite, $I_{Ti2Ni}/I_{TiNi(B2)}$, among all the quenched samples, it is possible to recognize a minimum for a film thickness of 800 nm while the furnace cooled sample shows a value closer to that of Sample D, the thicker in the batch. This could be an indication that in textured TiNi austenite the growth rate of the Ti$_2$Ni precipitates is significantly slower compared to the case of non textured grains.

### 3.5.1.3 The effect of heat treatment

Some interesting conclusions can be drawn about the correlation between film thickness and texturing of the films after the proposed heat treatments. The fact that the lateral grain size does not significantly change with the heat treatment nor with the film thickness may suggest that incubation and nucleation rate in all the samples are comparable and that after the complete crystallization of the amorphous films, no further lateral grain growth took place. As mentioned in section 4.1, this is a further hint that leads us to hypothesize that due to the relatively high crystallization temperature chosen, a first nucleation of a non-stoichiometric TiNi-like phase took place followed by a fast columnar growth in all the regions of the samples [46], and that only
in a second moment an eventual secondary nucleation and growth of different phases within the same grains happened [47]. This mechanism would explain the extremely uniform morphology of the grains in all the annealed samples yet with so different phase compositions and textures.

3.5.2 Mechanical properties

A qualitative correlation between mechanical properties and phase composition was observed and in particular a correlation was found between hardness and R-phase rich regions, considerably softer than the surrounding areas. On the other hand, only trends can be reported about the regions composed of TiNi austenite and martensite due to the non negligible concurrent presence of hard compounds of unknown mechanical properties. It shall be remarked that a clearer trend among all the samples was found in the $H$ plots while a less straightforward pattern is given by the $E_r$ plots. This is maybe due to the well known tendency for $E_r$ to be more sensitive to factors such as film thickness and experimental procedure than $H$, which is usually considered as a more “robust” parameter for thin film characterization. Hardness is indicative of the microstructure of materials since it is related to their plastic behaviour. Due to these reasons, it is not possible to extrapolate absolute values for $H$ and $E_r$ of the pure phases observed in the samples but it is reasonable to hypothesize a significant difference in hardness between
the equiatomic TiNi intermetallic (austenite, R-phase and martensite) and the other non equiatomic intermetallic phases. In all the samples, the regions showing the highest \( E_r \) values are always situated towards the Ti-rich regions of the samples and are associated with the highest amounts of non-equiatomic intermetallic phases (mostly Ti\(_2\)Ni), followed by those richer in austenitic phase. The Ti rich regions of the samples, with a strong presence of Ti\(_2\)Ni phase, show an elastic modulus of up to 155 GPa while on the opposite side (Ni rich region, TiNi\(_3\) and Ti\(_3\)Ni\(_4\) dominant phases), values within 110 GPa and 130 GPa were found. An indication of the microstructure of Ti\(_2\)Ni comes from the comparison of the same regions in samples B and C, Fig. 3.6d and 3.6f. The different intensities shown in the MAXRD plots in Fig. 3.3b and 3.4b for the peaks related to Ti\(_2\)Ni phase may indicate a coarser microstructure of Sample C, due to the slower cooling from annealing, resulting in a reduced hardening effect on the austenitic matrix common to both samples. The comparison of the MAXRD plot in Fig. 3.4b (first row) with the corresponding \( E_r \) map in Fig. 3.6e shows how the increase in Young’s modulus is proportional to the relative increase in Ti\(_2\)Ni fraction. The relatively high value for \( E_r \) (150 GPa) recorded in Sample B in the region with higher amounts of textured TiNi austenite, Ti53.5Ni40Cu6.5, although lower than the absolute maximum found in Sample C, where this phase is mixed with the harder Ti\(_2\)Ni, could be explained with a hardening of austenite due to a possibly smaller grain size. Martensite rich regions always showed the lowest values for elastic modulus (100-110 GPa). For what concerns the hardness
it is interesting to note that the softest spots in every sample always coincide with the regions where the transition between austenite and martensite takes place, which are richer in the pre-martensitic phase (R-phase), with a hardness value ranging from 5 GPa to 6 GPa. Both $E_r$ and $H$ found in the austenite and martensite rich regions in all the samples are in agreement with the values reported in literature [48-51], and the lower values for $E_r$ and $H$ found in the transition regions (R-phase rich) are also qualitatively compatible with the trends reported by Sugimoto et al. [50]. The measured values for $E_r$ and $H$ in the regions, where the TiNi phases (B2-R-B19') are dominant, are also in good agreement with those reported in literature [2, 48-50, 52]. The unusually low values for both $H$ and $E_r$ measured in Sample B, Fig. 3.6c-d, around a composition of Ti39.5Ni53Cu7.5 are quite close to the values found in the same region of the non annealed Sample E. This fact, together with the low signal shown in the MAXRD plot for the same region, suggests the possibility of the presence of a significant residual amorphous fraction around this spot. In Sample C, the hardest region appears to be on the martensitic side of the mapped area. There are several possible explanations for this fact including a significant presence of hard micro-precipitates, grain size (Hall-Petch) effects and film thinning at the borders of the sample. Nevertheless, as pointed out before, it is difficult to give a quantitative estimate for the contribution of each one of these phenomena due to $i$) the high number of parameters involved and $ii$) the lack of detailed nanoindentation literature data for all the observed phases (neither
in bulk nor in thin film form). At this purpose, a detailed study of the main intermetallics (other than TiNi) of this binary system would be required. While the results of nanoindentation experiments suggest a relationship between the mechanical properties of the films, their phase composition and microstructure, it was not possible to find a trend regarding the effects of texture.

3.6 Conclusions and outlook

In this study, thin films of compositionally graded Ti-Ni-Cu based alloys of different thickness and different thermal history have been characterized and compared. It has been shown that phase composition, microstructure and texture of the films can be significantly modified using Cu alloying, heat treatments and film thickness. A threshold value in film thickness between 350 nm and 800 nm appeared to be critical for the triggering of the texture in the austenitic phase. Multi-Axial XRD has been employed to achieve a qualitative phase analysis and crystallographic texture in this kind of samples. Significant differences in terms of phase composition, texture and mechanical properties have been evidenced although further and more focused studies are required to clarify the thermomechanical behaviour of such alloys in the case of different thermal treatments and in a wider range and/or improved detail concerning film thickness. The copper content has been found to have an influence on the microstructure of TiNi austenite, R-phase and martensite. Film thickness has been observed to be important in the determination of the
texture of austenite, probably through the modulation of the stress state of the films deriving from the production method. The cooling mode following the crystallization heat treatment seems to be correlated to a change in the texture direction of the austenite and in the microstructure of the resulting R-phase. Nanoindentation evidenced significant differences in the mechanical properties within each film and among all the films, mainly in function of thermal history and phase composition. Studies in more focused compositional ranges based on these preliminary results have been started with the aim of correlating the observed differences in microstructure and shape memory properties of the films. Moreover, to reach a better understanding of the exact evolution of phases and microstructures in the time-temperature domain during the crystallization process and the subsequent cooling to room temperature, it would be interesting although extremely time consuming to perform a complete crystallographic characterization of the samples described in this work using a diffractometer equipped so to allow the same kind of measurement at different temperatures. Nevertheless, due to the relatively long measurement time, we think that the very same setup we used for the present study would be unsuitable to follow the crystallization of the film with the due resolution in the time domain, and therefore a simpler XRD rocking-curve on selected peaks or a synchrotron based experiment should be preferred. Some literature about experiments using in situ traditional XRD scans [53] or TEM-based electronic diffraction together with sample heating is reported [25] but due to
the sample preparation procedure and to the much localized nature of this technique it is difficult to compare these results with the ones shown in the present study. This study shows that metallurgical treatments and size effects have a strong influence on phase composition, microstructure, crystallography and mechanical properties of TiNiCu based shape memory alloy thin films. Consequently, an upscaling of complex alloy systems, as developed by a combinatorial thin film approach, to bulk systems requires a fundamental understanding of size effects and scaling laws.

3.7 Acknowledgments

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3.8 References


[29]  PVD Products Inc., 231 Andover Street Wilmington, MA 01887, United States of America.


4 A combinatorial study on the influence of elemental composition and heat treatment on phase composition, microstructure and mechanical properties of Ni-W alloy thin films


4.1 Abstract

Ni-W alloys are promising materials for applications where mechanical stability at relatively high temperature is required. A series of Ni-W based thin films in a broad compositional range was produced using magnetron sputtering and subsequently annealed. Microstructure and phase composition were characterized by means of X-Ray Diffraction and TEM while the mechanical properties were assessed using nanoindentation. The results showed that the microstructure and the mechanical properties of the films are strongly influenced by the presence of intermetallics. An important finding is that around 25 W at% the equilibrium between the softening produced by grain growth and the hardening caused by the formation of intermetallic
phases, stabilizes the hardness of the films for a heating cycle representative of a high-temperature (N)MEMS application. Moreover, it has been found that the range of existence of all the detected phases appears to be significantly extended, regarding elemental composition, compared to the corresponding equilibrium phase diagram.

4.2 Introduction

The growing number of industrial applications for Micro and Nano Electro-Mechanical Systems (MEMS,NEMS) require new, high-performance materials with an extended range of properties [1, 2]. At this purpose there is an increasing demand, and therefore research effort, for materials able to withstand relatively high temperatures maintaining good mechanical properties [3, 4]. Pure nickel is already employed in the production of many micro-systems but the instability of its microstructure at intermediate and high temperatures is a limiting factor for devices operated in such conditions [5]. One possible solution to improve the performance of Ni in these conditions is the alloying with other elements, especially high-melting metals and, in this direction, Ni–W alloys are considered among the most promising ones. The addition of W in different amounts has been used to stabilize the microstructure of this material at high temperatures, although the combination of effects produced by the alloying are not always completely positive. As an example, an excessive reduction in grain size is reported to produce an
inverse Hall-Petch effect, thus weakening the mechanical properties of the system [6, 7]. Another negative effect reported in literature is the reduction in the ductility and the cracking of the films, especially for relatively high tungsten contents [8]. Among all the existing forming procedures for MEMS, the LIGA process (acronym from the German words for lithography, electroplating, and molding) is considered the most efficient in both performance and economicity making it the most interesting technique for mass production of high precision micrometric parts. The materials employed in the LIGA process are usually applied using electroplating. While many results for electro-deposited Ni and Ni-W alloys are reported in literature [1-12], a lesser amount of works are available in the case of thin films produced by means of physical vapour deposition (PVD). While electroplating is an efficient and relatively inexpensive method to produce conformal coatings, it may bring up several restrictions e.g. regarding substrates (it is a wet process), possible film composition (not all materials/alloys can be electrodeposited), layer uniformity, pre-processing of the molds (a seed layer is required for electric conductivity) and, not least, environmental issues concerning the chemicals used in the process. Other techniques, such as chemical or physical vapour deposition (CVD, PDV), are an interesting alternative to electrodeposition in the LIGA process for many aspects. Vapour deposition techniques allow the deposition of materials of virtually any composition on any kind of substrate, with little substrate preparation, reasonable coating speeds and in an extended range of temperatures. In this
work, a combinatorial study on submicrometric Ni-W alloy films with compositions within 0-85 at% W, prepared by means of magnetron co-sputtering is reported. The films were characterized by means of EDX, TEM, FIB/SEM, XRD and nanoindentation, both in the as-deposited state and after annealing at 800 K for 1 h. The results gave interesting insights about the effects of W addition and thermal history on the microstructure of the material and about the correlation between the microstructure and the mechanical properties of the films.

4.3 Experimental details

In the following of this report, we will refer to elemental composition, always in atomic %, as, e.g.: Ni45W55 and to stoichiometric compounds as, e.g.: Ni₄W.

4.3.1 Sample production

Thin film samples were produced in a combinatorial mode using a PVD Products sputtering device equipped with two magnetron guns holding the Ni and the W targets, installed below the substrate (sputter-up configuration), on a vertical plane orthogonal to the substrate surface and passing by a diameter of the same, with a target-to-substrate distance of about 145 mm. The principal axis of each gun is tilted 35° off the normal to the substrate holder and, additionally, the gun heads can be independently further tilted to control the compositional spread of the two elements over the sample.
surface. The chamber allows the in-situ thermal annealing of the samples by an array of IR lamps. A more detailed description of the deposition setup was given elsewhere [13]. As a substrate, single crystal Si wafers, (100) oriented, 3" diameter, 380 μm thick with 50 nm SiO$_2$ plus 50 nm Si$_3$N$_4$ diffusion barrier was used. The base pressure in the vacuum chamber of the sputtering equipment was always better than 7 μPa and the sputtering pressure for all samples was kept at 1.3 Pa. Sputter rate and film thickness homogeneity were determined by profilometry on test samples and after the sputter rate determination, the desired film thickness of 500 nm was achieved by timing the deposition process. The sputtering parameters (DC Power and magnetron tilt for both target materials) were optimized to cover different regions of the Ni-W binary system with a reasonably homogeneous film thickness (± 10%) over one sample and the whole explored compositional range was covered by means of 4 samples (with a certain overlap in composition). The as-deposited samples were used to evaluate the properties of the films prior to any thermal treatment. With the aim of studying the influence of temperature on the microstructure of the films, a copy of every sample was annealed in vacuum (always better than 70 μPa) for 1 h at 800 K, deemed to be representative of the extreme temperature cycle that an electronic or MEMS device can stand in normal service conditions. After annealing, all heat treated samples were allowed to freely cool in vacuum (cooling rate of approximately 20 K/min).
4.3.2 Crystallographic characterization by means of X-Ray Diffraction

Multi-Axial X-Ray Diffraction (MAXRD) was used to study phase composition and texture of the films using a PANalytical X’Pert Pro™ XRD system equipped with a PLXcel™ line detector, a MRD™ Euler cradle and mono-capillary X-ray lenses with 0.5 mm diameter. The use of X-Ray focusing optics allowed the measurement of spots with a diameter of about 0.5 mm (slightly varying with the source to substrate angle). It is worth to note that, to avoid an unreasonable duration of the measurements, the measurement parameters (exposure time and angular resolution) were adjusted to achieve a maximum measuring time per spot of around 6 hours. With this aim in mind, the angular ranges (35°<2θ<65° and 0°<ψ<65°) were chosen to include the main reflections of the phases deemed to be possibly present in the films (Ni, Ni₄W, NiW, NiW₂ and W) and a reasonable amount of off-plane texture components. The representation of the signal intensity (I) vs diffraction angle 2θ and tilt angle ψ, called the “orientation plot” (Fig. 4.1a), can be used to evaluate in a non destructive way local physical properties of the films such as stress state, grain size, grain geometry and texture for every phase detected. The interpretation of the orientation plots was performed by fitting the signal intensity I vs 2θ using a gaussian distribution function:

\[ f(x) = k + I \cdot e^{-\frac{(x-x_0)^2}{2s^2}} \]

where I stands for the peak maximal intensity, \( x_0 \) represents the peak center (along the 2θ axis), \( s \) is proportional to the peak
width and $k$ is the “vertical” offset of the peak base. A further fit of $l(\psi)$, this time parallelly to $\psi$ tilt, keeping $2\theta$ fixed in the position of the peak maximum, and again using a gaussian distribution, provides an estimate of the texture width of the phase in exam; a constant value of $l(\psi)$ over the whole range of tilts was interpreted as a non textured film. The application of the fitting coefficient $s$ into the Scherrer equation: $d = \frac{k\lambda}{\beta \cos(\theta)}$, with $\beta \approx 2.355 \cdot s$,

$\lambda = K_{\alpha,Cu} = 0.1542 \text{ nm}$ and $k = 0.9$, gave an estimate of the average size of the crystalline domains within the films. The authors are aware that in this range of grain size it would have been more appropriate to use the Warren-Averbach approach [14] rather than the Scherrer method, unfortunately the experimental setup used in the diffraction experiments did not allow the collection of a sufficient number of peaks to apply it. The “powder like plot”, derived from the “orientation plot” by integrating the intensity along the $\psi$ direction, was used to estimate the local phase composition and in general to compare the data collected in the thin films with the existing databases for powder diffraction spectra.
4.3.3 Morphology characterization by means of Scanning Electron Microscope (SEM), Focused Ion Beam (FIB) and Transmission Electron Microscope (TEM)

The surface of the films was imaged using a FIB/SEM (dual beam Carl Zeiss NVision 40). While the SEM was used to image the surface features, the FIB/SEM was employed to cut trenches in the films to determine the film thickness and sub-surface morphology. Moreover, since crystalline and amorphous fractions are expected to show a difference in ion-sputtering rate, a low-energy (10pA@30kV) ion-sputtering of the film surface was performed to evaluate the state of crystallization of the samples. To allow the imaging in the TEM, two 50 nm thick Si$_3$N$_4$ membrane windows were coated following the same procedure described for the main samples with the only difference that the process was timed to deposit a total thickness of about 100 nm (to achieve TEM transparency) and the compositions of Ni75W25 and Ni50W50 were chosen. The membranes were then annealed at 800 K for 1 h as for the other samples. The transmission electron microscope used in this work was a Philips CM 200 STEM equipped with a tungsten filament and operating at 160 kV. Samples were mounted on a double tilt holder. Images were taken with a Gatan 2x2 k CCD camera. All diffraction experiments were based on the same calibration procedure: (i) calibrating the TEM / CCD with a nano-crystalline Au-sample, (ii) normalizing all diffraction data from the Ni-W thin films to the characteristic W (110) reflection, assuming for W a lattice
parameter $a_0 = 0.3165$ nm. Convergent beam diffraction patterns were always compared to a selected area diffraction ring pattern taken at unchanged microscope settings, except the necessary change, centering of the condenser aperture and opening the beam from convergent to parallel.

4.3.4 Mechanical characterization by nanoindentation

Nanoindentation measurements were performed using a TriboIndenter (Hysitron Inc, USA) with a Berkovich tip in load-control mode using a partial-unloading function consisting of 7 cycles, up to a maximum load of 10 mN. The measurement were performed in the same spots where the XRD characterization took place. Every unloading segment of the force-displacement curves was analyzed by the Oliver-Pharr method [15], giving an estimate of the mechanical properties in function of the indentation depth. Every measurement position was probed with 10 indentations and the results were averaged to get a statistically significant value for both hardness ($H$) and reduced elastic modulus ($E_r$).
4.3.5 Elemental composition mapping by Energy-Dispersive X-ray Spectroscopy (EDX)

EDX maps of the samples were performed using a CAMSCAN SEM Series 4 equipped with a Baker Hughes Noran Instruments EDX detector. The EDX measurements were carried out at an acceleration voltage of 20 kV and an acquisition time of 60 s on a 10 μm square window, placed in the same positions corresponding to the XRD and nanoindentation measurement spots.

4.4 Results

4.4.1 Crystallographic characterization by means of Multi Axial X-Ray Diffraction (MAXRD)

4.4.1.1 Crystallinity and phase composition

The results of Multi Axial X-Ray diffraction mapping of the Ni-W films are summarized in figure 4.1a,b and in table 4.1.
Fig. 4.1a MAXRD orientation plots representing the four characteristic regions covering the behavior of the whole explored compositional range. In the as-deposited films, it can be seen how the alloys are crystalline at the extremes of the explored elemental composition range (0<W<85 at%) while around the region of composition Ni50W50 a progressive amorphization appears. The annealed samples are crystalline for all the elemental compositions. No significant texture is visible in any of the identified phases except the β-W phase in the as-deposited samples, which shows a moderate (100) texture.
Fig. 4.1b MAXRD powder-like plots representing the four characteristic regions covering the behavior of the whole explored compositional range. In the as-deposited films an increasing amorphization for the compositions close to Ni50W50 can be seen. The annealed samples show fully crystalline patterns in all the explored compositional range. Comparing the Ni-rich alloys before and after heat treatment, a peak narrowing due to grain growth can be noticed.
Table 4.1
Summary of XRD characterization

As-deposited films:

<table>
<thead>
<tr>
<th>Region name:</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>W, at%</td>
<td>0-25</td>
<td>25-50</td>
<td>50-75</td>
<td>75-100</td>
</tr>
<tr>
<td>Grain Size, nm:</td>
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<td>5-10</td>
<td>Amorphous</td>
<td>15-20</td>
</tr>
<tr>
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<td>Weak</td>
<td>None</td>
<td>Moderate</td>
</tr>
<tr>
<td>Main Phases:</td>
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<td>Ni, struct. A1, sp.gr. Fm-3m</td>
<td>None</td>
<td>β-W, str. A15, s.g. Pm-3n</td>
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</table>

Annealed (800 K, 1 h) films:

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<tr>
<th>Region name:</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
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</thead>
<tbody>
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<td>W, at%</td>
<td>0-25</td>
<td>25-50</td>
<td>50-75</td>
<td>75-100</td>
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<tr>
<td>Texture:</td>
<td>Moderate</td>
<td>Weak</td>
<td>None</td>
<td>Weak</td>
</tr>
<tr>
<td>Main Phases:</td>
<td>Ni, str. A1, s.g. Fm-3m</td>
<td>Ni₆W, str. D₁₅, s.g. I₄/m</td>
<td>Ni₆W, str. D₁₅, s.g. I₄/m</td>
<td>α-W, str. A2, s.g. Im-3m</td>
</tr>
<tr>
<td></td>
<td>α-W, str. A2, s.g. Im-3m</td>
<td>Ni₆W, s.g. P₂₁₂₁₂₁</td>
<td>Ni₆W, str. D₁₅, s.g. I₄/m</td>
<td></td>
</tr>
</tbody>
</table>

The analysis shows that, with increasing additions of W, the alloy gradient can be divided in four main regions: a) W₀-W₂₅, b) W₂₅-W₅₀, c) W₅₀-W₇₅ and d) W₇₅-W₁₀₀ for both the as-sputtered and the annealed states. For what concerns the as-sputtered films, the results from the regions a), b) and d) indicate that the material in these ranges of compositions is found in a (at least partially) crystalline state even without the help of a heat treatment, while in the region c) only a diffuse diffraction ring typical of amorphous materials is visible. Moreover, the crystalline regions close to the pure Ni and
to the pure W extremes of the gradient show a texture, although weak. Regarding the phase composition of the crystallized regions in the as-deposited samples, Ni(W)$_{ss}$ (fcc) solid solution on the Ni-rich side of the gradient and $\beta$-W on the W-rich side are present. At a composition of Ni$_{75}$W$_{25}$ a broad peak is superimposed to the amorphous diffraction ring, corresponding to the Ni(W)$_{ss}$ (111) or to the Ni$_4$W (211) reflection, suggesting the presence of a supersaturated Ni(W)$_{ss}$ or the onset of crystallization of Ni$_4$W. Regarding the annealed samples, all the explored regions were found in a crystalline state, showing a weak to moderate texture in the same region that were found textured in the as-sputtered samples. Compared to the as-deposited samples, after the heat treatment, a wider variety of phases appears in the whole analyzed range. While the Ni-rich region (a) maintains the same fcc-Ni composition, the intermediate regions (b,c) show a mixture of intermetallics, Ni$_4$W and NiW, always accompanied by the presence of $\alpha$-W. The W-rich side (>75%) of the gradient is mainly composed of $\alpha$-W with minor amounts of Ni$_4$W.

**4.4.1.2 X-Ray Diffraction data fitting**

The analysis of the diffraction data by means of gaussian fits allowed the evaluation of grain size and stress state of the films, before and after heat treatment. It shall be noted that not all the diffractograms produced usable fit results, mostly due to the absence of valid signal or to excessive peak broadening in the (partially-)amorphous regions. Due to these reasons, and to
improve the comparability of the results, it was decided to choose the signal coming from phases with significant peaks extending over the broader elemental composition span in the samples, and in particular the Ni(W)_{as} (111) peak for the as deposited films and the α-W (200) peak for the annealed ones. Figure 4.2 shows the variation of grain size as a function of the W content of the alloys, with a simplified equilibrium binary phase diagram for Ni-W superimposed.

Fig. 4.2 Plot of grain size derived from the fitting of selected peaks of the XRD scans (Scherrer method). Grain size for as-deposited materials was derived from Ni (111) peaks while W (200) peaks were used for the annealed samples. As a guideline, the boundaries of existence of the stoichiometric phases in the Ni-W equilibrium binary phase diagram are reported on the top of the graph. Please bear in mind that our films are in a non-equilibrium state.

As expected, the grain size for the annealed alloys is always higher compared to the as-deposited films and it shows a trend depending on the elemental/phase composition. In the case of as-deposited films, it can be
seen how the grain size decreases with the increasing W content in the alloys to the limit of amorphization above 30 at% W, in reasonable agreement with literature [7, 9, 16, 17]. Concerning annealed films, and considering the superimposed phase diagram, it can be noted that in the proximity of the composition corresponding to 70 at% W the grain size shows a minimum. The residual stress state of the films was also calculated combining the diffraction data with the Young’s modulus obtained from the nanoindentation experiments. As shown in figure 4.3, a less clear pattern in the dependence of stress from W content is present.

Fig. 4.3 Plot of residual stresses derived from the fitting of selected peaks of the XRD scans (Sin²(ψ) method). Stresses for as-deposited materials were derived from Ni (111) peaks while W (200) peaks were used for the annealed samples. As a guideline, the boundaries of existence of the stoichiometric phases in the Ni-W equilibrium binary phase diagram are reported on the top of the graph. Please bear in mind that our films are in a non-equilibrium state.
The main difference in the films before and after the heat treatment is that as-deposited films show low residual stresses without a clear trend (+/- 0.5 GPa) while a tensile state (+0.5 to +1.5 GPa) is calculated for the annealed alloys, as expectable in the case of crystallization of (partially-)amorphous materials.

4.4.2 FIB/SEM characterization

SEM images of the surface and of the subsurface features of as sputtered (Fig. 4.4) and annealed (Fig. 4.5) samples show how the crystallization state and the morphology of the films is influenced by their local elemental composition and thermal history. Trenches 4 x 2 μm wide and 1 μm deep were cut by means of FIB, keeping all the process parameter identical for every spot, and their edges were imaged by means of SEM. In the lower row of pictures in figures 4.4 and 4.5, the effects of preferential sputtering of the same spots where the trenches were cut are also shown.
Fig. 4.4 SEM imaging of FIB cut trenches (a,b,c) and low-current surface erosion (d,e,f) of high-W as-deposited films. In these images it is displayed how the increasing amount of amorphous phase produces a weakening in the ion-sputtering (FIB) resistance of the alloys. The brighter spots represent crystalline Ni₄W, showing higher sputtering resistance than the surrounding matrix.

Fig. 4.5 SEM imaging of FIB cut trenches (a,b) and low-current surface erosion (c,d) of high-Ni annealed films. Compared to the as-deposited films, the annealed alloys show a sharper FIB cut and columnar structure, derived by the higher resistance to ion milling. In the film annealed at higher temperature and longer time, a coarser structure is visible.
For the as deposited films, to validate the results coming from the XRD analysis and to investigate the resulting microstructures, the region above W 50 at% (amorphous to crystalline transition) was selected (Ni70W30, Ni60W40 and Ni50W50). Moreover, to demonstrate the evolution of crystalline films due to annealing, the Ni-rich region (W5) was imaged after two different heat treatments, (400 K, 1 h and 800 K, 6 h). Differences in the FIB cut on the edges of the trenches show a substantially different behaviour for ion-sputtering in all the imaged spots. In the W-rich samples (Fig. 4.4), in the transition from lower to higher W content, the edge of the trenches changes from a rounded to a sharp profile and microstructures with increasing resistance to ion-sputtering are visible, embedded in the bulk of the films. In both Ni-rich annealed films (Fig. 4.5), the surface roughness looks significantly increased compared to the as deposited, and after the surface sputtering, columnar-like structures appear. In the film annealed at 800 K for 6 h, a coarser microstructure compared to the one annealed at 400 K for 1 h is visible.

4.4.3 TEM characterization

Samples of Ni75W25 and Ni50W50, 100 nm thick, deposited on 50 nm thick Si₃N₄ windows, both annealed at 800 K for 1h, were examined by means of bright field imaging (BF), centered dark field imaging (CDF), selected area diffraction (SAD), and convergent beam diffraction (CBD). Both samples are fully crystallized and show a morphologically similar fine grained
microstructure (Fig. 4.6). Grain size approaches an average of approximately 50 nm to 100 nm, which is three to six times larger than derived from XRD_{Scherrer} data for the thicker samples. Many grains are fragmented by internal boundaries; so e.g. often dense twinning is observed. The Ni75W25 sample is more homogeneous than Ni50W50 where grain size variation covers one order of magnitude from 20 nm to 200 nm. The BF grey scale contrast does not allow distinguishing safely between different phases on a pure morphological basis since it is a random overlay of diffraction and absorption contrast.

Fig. 4.6 Microstructure of Ni75W25 (a,b) and Ni50W50 (b,c) thin film after annealing at 800 K for 1 h. TEM bright field.
Clear evidence for the poly-phase nature of the samples is obtained from SAD patterns (Fig. 4.7) taken with a wide selecting aperture so that several thousand grains were illuminated by a parallel electron beam.

![Fig. 4.7 Electron diffraction pattern from the microstructure in Fig. 4.6a and 4.6c. Selected area diffraction (SAD) including an average of 3000 grains. In Fig. 4.7a, intensity from three different phases: Ni, W, and Ni₄W. In Fig. 7b, Intensity from five different phases: Ni, W, Ni₄W, NiW, and "X" (unidentified cubic, see text). Indexing for major lines only.](image)

Diffracted intensity of the following phases is observed: Ni(W)$_{ss}$, α-W, and Ni₄W (for both Ni75W25 and Ni50W50), plus NiW (for Ni50W50 only). In Ni50W50 a further phase of unknown composition, therefore denoted here as X, was detected: SAD and CBD experiments support that the crystal structure of this phase is fcc, space group Fd3m, with a large lattice parameter $a_0 = $
1.09 nm corresponding to three times the lattice parameter of Ni(W)\textsubscript{ss}. A detailed study on this phase X will be communicated in a separate publication. The SAD patterns (Fig. 4.7) do not contain any further unidentified diffraction rings, and for all mentioned phases complete sequences of reflections are observed. Therefore, this result leaves no open space for speculations regarding the eventual presence of further phases. Nevertheless it cannot be absolutely excluded that other minority phases, which escaped detection, might exist in minor amounts. Due to similar interplanar spacings of the different phases, there are typically close coincidences of diffraction rings in SAD patterns (Fig. 4.8).

![Fig. 4.8 SAD patterns from NiW7525 showing the fine structure of diffraction rings at high camera length. a) Overview. b) Detail. The marked lines show the close coincidence of reflections from Ni, W, and Ni\textsubscript{4}W.](image)
Examples are (i) Ni (111) and Ni₄W (211), (ii) Ni (200), Ni₄W (130), and Ni₄W (002), (iii) Ni (220), W (211), Ni₄W (420), and Ni₄W (132), (iv) Ni (311), Ni₄W (501), and Ni₄W (312). Such close coincidences may result in ambiguities in phase identification. However, with the exception of Ni, all phases can be unambiguously identified from at least two free standing characteristic diffraction rings. These are: for W (110), (200), and (310); for N₁₄W: (110) and (101); for NiW (131) and (040), and for X: (111), (220) and (311). With the identification of Ni the situation is not so obvious, even though highly probable because the complete sequence of 8 diffraction rings from (111) up to (420) is observed. Any remaining ambiguity can be removed by CBD of single grains, since CBD combines information about interplanar spacings with symmetry information (Fig. 4.9). Two CBD patterns (Fig. 4.9a,b) of two different grains in Ni₅₀W₅₀ are shown together with the SAD calibration pattern (Fig. 4.9c). Symmetry and dimensions of the (point)-patterns are consistent with Ni (beam directions <110> and <111>, respectively), but inconsistent with any of the other detected phases. CBD was also successfully applied to confirm the existence of Ni in Ni₇₅W₂₅, and of W in both Ni₇₅W₂₅ and Ni₅₀W₅₀. Such experiments require controlled alignment of low-index directions parallel to the electron beam and are, though basically standard in TEM, difficult to perform in practice with the actual fine grained samples.
The description so far refers to the poly-phase grain-grain structure of the samples. Concerning single grains, CBD from single Ni grains in Ni75W25 revealed also evidence for ordering phenomena. Figure 4.10 shows two CBD patterns from two different, but very close, areas of the same Ni grain, obtained by a slight shift (20 nm) of the electron beam. Strong spots are Ni reflections, weak spots are superstructure reflections. Obviously, there are two different areas within the same grain: a first one with one single domain orientation (Fig. 4.10a) and a second one with two symmetry-related domains (Fig. 4.10b). The primitive repetition period of the superstructure pattern is 1/5 Ni (420) (Fig. 4.10c) corresponding to the interplanar spacing for Ni4W (110). This phenomenon is coupled with the nucleation and formation of Ni4W within the Ni(W)ss. Since such ordering is not observed for all Ni grains, it can be
further concluded that two modifications of Ni(W)ss exist simultaneously: disordered and ordered.

![Fig. 4.10: Two [001] CBD patterns from ordering in Ni solid solution. a) One domain. b) Two symmetry-related domains. c) Schematic diagram explaining a) and b). The period of ordering reflections is 1/5 Ni <420> corresponding with Ni₄W <110>.](image)

Apart from phase determination, information concerning morphology, relative amount and spatial distribution of phases is important. Such information can be obtained by CDF imaging as illustrated in figure 4.11 for a selected area of the Ni75W25 sample. In the BF image (Fig. 4.11a) two grains are marked as 1 and 2. Figures 4.11b and 4.11d show SAD patterns from this area. Their overall appearance is different due to a slight sample tilt of 5° and a slight
sample shift, both necessary in order to obtain strong characteristic reflections which can be identified and discriminated experimentally to form the correlated CDF images (Fig. 4.11c, 4.11e). Grains 1 and 2 are obviously identified as Ni₄W grain (twinned) and as W grain, respectively. Basically, many experiments following this procedure may sum up, finally, to an almost complete description of the microstructure. Such research is currently in progress.

Fig. 4.11 Two examples of centered bright-field / dark-field TEM images from single grains in NiW₇₅₂₅. a) Bright field image with marked grains 1 and 2. b) and d) SAD patterns with selected reflections W (110) and Ni₄W (110). c) and e) correlated dark field images of Ni₄W and W grains.
4.4.4 Nanoindentation

In figure 4.12 the trend of hardness vs elemental composition is reported. The hardness decreases for Ni-rich alloys (W<25 at%) upon annealing and increases for higher W contents (W>25 at%). Moreover, for both as deposited and annealed alloys the hardness seems to develop following well defined trends, marked by the lines superimposed to the experimental points.

![Graph showing hardness vs elemental composition with zones 1 and 2 and shaded stripes for phases.](image)

Fig. 4.12 Plot of Hardness vs elemental composition. The superimposed lines are representative of the different slopes followed by the experimental points. Microstructure and phase composition ideally divide the diagram in two main regions, named Zone 1 and 2. In the bottom of the plot area we summarized the phases encountered in the films by means of shaded stripes. As a guideline, the boundaries of existence of the stoichiometric phases in the Ni-W equilibrium binary phase diagram are reported on the top of the graph. Please bear in mind that our films are in a non-equilibrium state.
For the sake of comparison with the results produced by XRD and TEM, in the lower part of the plot the phase composition of the samples is summarized by means of stripes shaded to simulate the trend for the amount of each phase. In figure 4.13 a Log/Log plot of the hardness values measured by nanoindentation against the grain size calculated from the XRD\textsubscript{Scherrer} measurements is reported. The results are shown in two groups coming from the XRD data of Ni(W)\textsubscript{ss} and \(\alpha\)-W reflections and in both groups the lines fitted through the experimental points show a slope close to the value predicted by the Hall-Petch theory for grain size hardening (-0.5).

Fig. 4.13 Log-Log plot of Hardness vs Grain Size. The superimposed lines, fitting the experimental points, reveal a good agreement with the Hall-Petch theory.
4.5 Discussion

The results coming from the compositionally graded films show significant trends regarding the effects of elemental composition and heat treatment on phase composition, grain size and microstructure of the films.

4.5.1 Phase composition

Alloyed films deposited by means of magnetron sputtering often show both non-equilibrium (metastable) phases and non-equilibrium phase compositions. Nevertheless, most of these features disappear after annealing. An unexpected result was the extended range of existence of the phases found in the annealed films compared to the equilibrium phase diagram. Two significant examples of this phenomenon are that α-W grains were found in the Ni75W25 films and Ni grains in the Ni50W50 samples. This finding shows that the conditions of strong non-equilibrium reported in previous works [16] for as deposited films are maintained even after the annealing treatment used in this work (800 K, 1 h) and, in general, that this heat treatment leads to the formation of all the equilibrium phases but not necessarily to the equilibrium phase composition. In our study, electron diffraction also revealed the presence of ordered Ni(W)$_{ss}$ solid solution in the Ni75W25 annealed samples and although some authors [17-22] already reported about this phenomenon, its origins are still debated and it would be certainly worth a further research effort in this direction. The metastable, textured β-W phase found in the as
deposited films could be explained by incorporation of process gas (Ar in this case), in agreement with the works of Djerdj et al. [23], Tang et al. [24] and of Bain et al. [25], who studied films produced with both PVD and CVD methods. Our study determined that the applied annealing treatment is sufficient to completely transform the original $\beta$-W in randomly-oriented $\alpha$-W. Although only reflections corresponding to Ni(W)$_{ss}$, $\alpha$-W, $\beta$-W, Ni$_4$W and NiW have been clearly identified in the XRD and TEM analysis, it cannot be excluded that also Ni$_3$W and NiW$_2$ could be present in the samples due to the fact that the reflections of both Ni$_3$W and NiW$_2$ are known to be difficult to be spotted since both fall very close to those of $\alpha$-W and NiW, as reported by Arapova [26] and by Zhu et al. [10], respectively. It is interesting to note that the phase diagram of the Ni-W binary system is still debated [27]: many phases were found to be metastable [28] and in some cases even the existence itself of Ni$_4$W, NiW and NiW$_2$ is under debate [29].

4.5.2 Microstructure and mechanical properties

As shown in figure 4.12, the increase in hardness against W content develops in a segmented trend which can be explained combining the results of nanoindentation with those coming from XRD/TEM regarding phase composition and grain size. The first region, called “Zone 1” in figure 4.12, is composed only by a Ni(W)$_{ss}$ where, according to Schuh et al. [7] the hardening effect provided by the solid solution (W < 15 at%) should be
negligible compared to the Hall-Petch effect (intrinsic $H_{Ni} = 800$ MPa, $\Delta H_{Ni(W)ss} = 40$ MPa, nanocrystalline $H_{Ni} > 7$ GPa). Moreover, the plot shows that the hardness difference between as-deposited and annealed Ni-rich samples is reduced and possibly caused only by grain growth [12]. Consequently, the reduction in grain size for increasing W contents showed in figure 4.2 in the corresponding compositional range could account for the big part of the hardening in this region, for both as-deposited and annealed films. In the area of the plot after $W > 25$ at%, called “Zone 2” in figure 4.12, it can be seen how the hardness continues to grow, with two different slopes, in both the as-deposited and annealed state and showing a general increase in the whole compositional range after the annealing treatment. Referring to as-deposited films, in the segment marked with an ellipse ($25 < W$ at% $< 60$), the presence of a substantial amount of amorphous phase in the film, as found by XRD, can explain the limited variability of hardness, as shown by the same authors of this work for Ni-Ti amorphous alloys [13]. Moreover, due to the limits of the Hall-Petch effect towards strongly reduced grain sizes, even the contribution of the grain boundary strengthening would be increasingly reduced in the as-deposited films above 40 at% W [30]. The increasing amount of crystalline $\beta$-W would explain the steep increase in hardness in the rest of the explored compositional range. The fact that the average grain size of the annealed films in the “Zone 2” is one order of magnitude bigger than those encountered in “Zone 1” suggests that the strong increase in hardness observed in this region should be attributed mostly to the different phase composition of the
films rather than to Hall-Petch effect [9]. This is confirmed by the observation that the fields of existence of the remaining phases found in the samples are roughly corresponding to the changes in slope visible in this diagram. A very interesting effect observed in the nanoindentation results is the inversion in the softening/hardening effect produced by the annealing at a composition close to Ni 25 at%. Our explanation is that at this composition, the softening produced by grain growth is balanced by the hardening caused by the crystallization of intermetallic phases deriving from both the supersaturated crystalline Ni(W)ss solid solution and the amorphous fraction. Regarding the determination of the grain size, TEM bright field images in figure 4.6 may suggest an estimate for the grain size which is on average 4 times the value calculated from XRD_{Scherrer} data. This discrepancy could be explained by a difference in crystallization and grain growth between the films used for the TEM characterization and those employed in all the other characterization techniques, due to their different thicknesses (~100 nm vs ~500 nm) and substrates (~400 μm thick Si vs 50 nm thick Si3N4). These differences may have generated slightly dissimilar temperature distributions during annealing and cooling, stress states and diffusion conditions for the two sets of samples which could account for the coarser grain size of the TEM samples. Another cause for the two different grain size estimates could come from the fact that XRD peak broadening is influenced not only by grain boundaries but also by subgrain boundaries, twinning, and finally all kind of structures reducing the extent of crystallographic periodicity. Examples of these defects were found in
the TEM analysis. In any case, for the purpose of correlating microstructure with mechanical properties we deemed more appropriate to consider as average grain size the one coming from the XRD\textsubscript{Scherrer} data analysis (thicker films, same samples used in nanoindentation) rather than that from TEM images (thinner samples). The data-fits shown in figure 4.13, combining information coming from nanoindentation and grain size, result in good agreement (-0.5±0.1) with the expected dependency of plastic properties with grain size [7, 11, 31]. The Hall Petch coefficient $K$ calculated from the same fits is compared with those found in literature for similar materials (Table 4.2).

Table 4.2
Hall-Petch Coefficients comparison (Experimental - Literature)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Source</th>
<th>Production Method</th>
<th>Mechanical Characterization</th>
<th>Grain Size Characterization</th>
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<tbody>
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<td>Ni</td>
<td>[32]</td>
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<td>Tensile Tests</td>
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<td>[7]</td>
<td>Electroplating</td>
<td>Nanoindentation</td>
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<td>This work</td>
<td>Magnetron Sputtering</td>
<td>Nanoindentation</td>
<td>XRD</td>
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<tr>
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<td>Nanoindentation</td>
<td>TEM</td>
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</table>
The coefficient K calculated in our work for Ni(W) as (the “Zone 1” in Fig. 4.12) using the grain size derived from XRD peak broadening was found in good agreement with the data coming from the work of Wang et al. [32] (8.7 GPa/nm$^{-1/2}$ vs 9.8 GPa/nm$^{-1/2}$ respectively), while the same coefficient calculated by us using a grain size estimate coming from TEM bright field images matches the data reported by Schuh et al. [7] (17.4 GPa/nm$^{-1/2}$ vs 18.7 GPa/nm$^{-1/2}$ respectively), the variation being probably due to the different experimental methods used to determine both mechanical properties and grain sizes. On the other hand, the Hall-Petch coefficients obtained in our work for the W-rich alloys (the “Zone 2” in Fig. 4.12) (80.4 GPa/nm$^{-1/2}$ with XRD data and 165 GPa/nm$^{-1/2}$ with TEM data) do not agree with the value (42.8 GPa/nm$^{-1/2}$) reported by Mathaudhu et al. [33] for pure W. In this case, the discrepancies between the K coefficients found in literature and those calculated in our work could be explained considering that the data from Mathaudhu et al. are related to pure W, while in our case the hardening effect produced by the Ni-W intermetallics could be predominant over the grain boundary strengthening.

4.6 Conclusions and outlook

This work showed that PVD deposited sub-micrometric Ni-W alloy thin films, exhibit non equilibrium phases in the as-deposited state and after the application of a thermal treatment non-equilibrium with regards to phase compositions are found. All the identified phases showed a significantly
extended field of existence, in terms of elemental composition, compared to the equilibrium phase diagram for the Ni-W system. Ordering in the Ni(W)ss and a possible new Ni-W phase were revealed by TEM analysis. It has also been shown how the stoichiometry affects the mechanical properties of these alloys in the shape of thin films. We evidenced how the evolution of the hardness in this family of alloys is dependent on phase composition; in particular, the behavior of the alloys was found to be dominated either by the presence of Ni(W)ss ("Zone 1", 0<W<25 at%) or by the presence of W and intermetallics ("Zone 2", 25<W<85 at%). In the “Zone 1” the main hardening effect is constituted by the Hall-Petch effect, and therefore a softening caused by grain growth is observed after annealing. In the “Zone 2” the primary cause for strengthening is given by the increased fraction of harder phases, whose onset during the thermal treatment produced a significant hardening of the films. The transition region between these two zones showed a reduced sensitivity of its mechanical properties to annealing, due to the balance between the described hardening and softening effects. We believe that further investigations should be performed to better characterize the surroundings of this composition (Ni75W25) to achieve the most effective stabilization effect of mechanical properties for high temperature applications.
4.7 Acknowledgments

The authors would like to thank Marianne Dietiker for the help in the interpretation of nanoindentation results, Dr. Noble Woo for the production of the preliminary samples, Susanne Köppl for her assistance in SEM, FIB and TEM imaging and Dr. Giancarlo Pigozzi for the useful discussions regarding TEM image and TEM diffraction pattern interpretation.
4.8 References:


5 Conclusion and Outlook

5.1 Experimental methods

Two new experimental methods for the study of thin films have been developed and successfully employed in this research: 1) a high-vacuum quenching method to be applied in the heat treatment of films potentially affectable by unwanted chemical reactions with atmospheric gases and 2) a new XRD technique allowing the study of textured multi-phasic films. The quenching method used in this work was used to study the influence of the cooling segment after a crystallization annealing of Ni-Ti-Cu alloys and it was proven to produce significant differences in the final microstructure and phase composition of the films. The Multi-Axial XRD technique improved the characterization of the films where the use of the traditional \( \theta/2\theta \) scan method with a single-point detector could produce a diffractogram where the peaks of one or more textured phases could be missing because of the preferential orientation of the crystallites. Obviously, the use of image plate detectors would entirely solve the problems but the majority of the X-Ray diffractometers available in metallurgical research labs are usually equipped with single-point detectors and large area image-plate detectors are still expensive and therefore uncommon other than in synchrotron based facilities. Although many interesting and potentially more powerful methods than the one we propose were described in recent publications [1, 2] we believe that
our procedure is more suitable for the employ in the field of routine combinatorial research being it economical (needing only a common X-ray diffractometer and no expensive and/or difficult to access facilities like a synchrotron) and easy to automate (needing only an euler cradle and a linear motion stage). Moreover even in the case where texture is not the main topic of the study, multiple XRD scans retrieved at different tilts may provide useful additional information about the system, compared to the traditional single scans. For example, applying Scherrer’s formula to all the scans, it is possible to get an estimate about the average geometry of the grains (columnar, spherical, plate-like) while the use of the $\sin^2(\psi)$ method provides an estimate of the local stress state of the material. Due to the high amount of information produced in all the automated measurement techniques utilized in this work, a very important role was played by information technology techniques. Custom made programs were written and were extensively used to pre-process, combine, analyze and visualize data coming from several instruments with different output standards and in particular: nanoindentation, XRD, EDX.

5.2 Material systems

The main finding of this work is that phase composition and microstructure of sputter-deposited thin films of a fixed elemental composition depend in a complex fashion on film thickness and thermal history. In particular it has
been shown that the equilibrium phase diagrams available from bulk alloys are only of limited use in the case of thin films due to the inherent conditions of strong non-equilibrium during the deposition of these materials. The direct solidification from vapor state allows the deposition of materials whose elemental composition and/or microstructure may be impossible to attain with traditional methods. In the present research, supersaturated solid solutions or even completely homogeneous, amorphous solid solutions of 2-3 elements were common in the as-deposited state. The interplay between crystallite nucleation, grain growth rate and strain vs surface/interface energy minimization, all function of film thickness, were used to explain phase composition and microstructure of the studied films. Higher fraction of interfaces (favoured nucleation sites) and limited stresses in the thinner films (<500 nm) determined the presence of smaller, non textured grains compared to thicker films (500<h<1000 nm) where the main driving force for crystallite growth and texturing is represented by strain energy minimization. As-deposited films were usually found in a crystalline state close to the pure element side of the compositional gradients (Ni > 80 at%, W > 80 at%) while in the intermediate compositions they showed amorphous fractions, supersaturated and/or metastable phases. Annealed films were always crystalline and they showed all the phases described in the equilibrium phase diagram but in non-equilibrium amounts so that it was common to find detectable amounts of a certain phase well beyond its equilibrium field of existence (α-W at Ni 75 at%). Regarding mechanical properties, significant
differences were found in the hardness of the two explored metallic systems. Although in both cases intermetallic phases were found to be an important hardening cause, in the Ni-Ti-Cu ternary system the austenite-(pre)martensite transition and in the Ni-W binary system the Hall-Petch effect provided additional degrees of freedom to the problem. In particular, in the Ni-Ti-Cu alloys it was shown that the regions rich in the pre-martensitic R-phase are significantly softer than the austenitic or martensitic regions, probably due to the conversion of the indenting stress to phase transformation (austenite $\rightarrow$ martensite). Ni-W alloys displayed an interesting trend for hardness as a function of thermal history and elemental composition, reflecting the two main hardening mechanisms: phase composition and microstructure. Until a composition of W 25 at% the prevalent hardening cause is the Hall-Petch effect, confirmed by a softening of these alloys after the heat treatment, while all W-rich alloys (W > 25 at%) showed an increase in their hardness after annealing. We believe that this property could be used as a stabilizing phenomenon for thin film materials where constant mechanical properties should be maintained at high temperatures. In any case we demonstrated that metallurgy of alloys in thin film shape can only partially rely on the scientific literature and on the technical data (e.g. TTT and CCT diagrams) collected for bulk materials. Under the scientific point of view it would be interesting to reach a detailed understanding of the behavior of alloys in reduced dimensions so to be able to predict their configuration after an arbitrary heat cycle and most of all to be able to exploit the peculiarities of
these materials and their production cycles to fabricate new and more performing alloys. Under the technical point of view, future technological applications of materials in reduced dimensions, and in particular thin films, will have the need for reference data to base design and development of products and processes. Nevertheless, due to the increased complexity of this class of materials, the build-up of specific databases will require the use of “extra-indexes” like: fabrication method (and related process parameters), film thickness and substrate material.

5.3 Outlook

In the framework of this thesis, two metallic alloys in the shape of thin film were investigated using a combinatorial approach showing the dependence of crystallographic, microstructural and mechanical properties from elemental composition, film thickness and thermal treatments. The work revealed that reduced dimensions produce strong effects on the metallurgical features of the alloys making existing knowledge on bulk alloys of similar composition difficult to apply in this field. This finding leads to the conclusion that further research on this topic should be carried out to clarify the effect of film thickness and heat treatment on a wider range of alloys and substrates.
5.3.1 Equipment

It is important to take into account that the laboratory equipment required for this specific research field is at the present moment in a relatively early stage of development and little “off-the-shelf” solutions are available at this purpose. Just to give an example, it was not possible to find on the market an oven for thin film thermal treatment and therefore, to perform the thermal treatments required for this research, the high-vacuum chamber and the heater of a sputtering equipment were used instead. An important contribution to future researches on controlled heating and cooling treatments in thin films could be achieved by building a specifically equipped oven/cooler benefiting from the experience gathered in the present work. The key features required for this project would be: high vacuum with residual gas analysis, accurate temperature control over all the surface of the sample and quenching capability. Desirable features would be the availability of electrical feedthroughs and line of sight flanges adequately fitted to perform in-situ analyses like XRD, electric resistivity or curvature monitoring of the samples.

Regarding the cooling capabilities of such a piece of equipment, due to the high-vacuum requirement, the use of convection heat transfer seems impossible, while the radiation mode is inadequate to achieve a rapid enough cooling of the samples. The only feasible way of cooling the films is represented by contact cooling, as shown in the results of the present work. Although far from technical perfection, the prototype employed in our research produced significant microstructural differences in the quenched
samples compared to their furnace-cooled counterparts and provided a proof of principle of the validity of this technique.

5.3.2 Combinatorial techniques

With the aim to study the highest number of paremeter variations in an time efficient way, it could be interesting to apply the concept of combinatorial studies to both elemental composition and to thermal treatments, using orthogonal gradients. One way of doing so could be by producing samples with a thickness gradient along one direction and applying to the same a differential heating/cooling treatment along an orthogonal direction. This could be achieved by means of an asymmetrical heating device (an array of IR lamps with different power applied to each of them) or by tilting the sample with regards to the heat source, provided an adequate (low) thermal conduction on the sample/substrate. Another interesting way of producing a graded annealing treatment would involve the use of a pulsed laser source and a scanning sample holder. Ideally, in-situ XRD and/or electric resistivity could be used to define the crystallization/phase formation temperatures. The described experimental set-up is without doubt a challenging endeavor and would require the design and the construction of a complex vacuum tight piece of equipment, but in our opinion its implementation would allow a significant improvement in the output capabilities of a research in this field.
5.3.3 Material systems

Regarding the material systems that would be interesting to investigate in more detail, both systems analyzed in the present work could be good candidates. We believe that especially the Ni-W binary system should be chosen, the main reason being that it would represent a simplified case compared to the Ni-Ti-Cu ternary system, where the combination of elements can produce a much higher and complicate set of interactions. In particular, it would be of extreme interest to investigate with improved detail the influence of the microstructure and of the mechanical properties in this binary system around the Ni 25 at% composition, to better understand the interactions of hardening and softening phenomena and to finally find an optimal composition for thermally stable films to be employed in technological applications. To study the effects of reduced dimensions on the behavior of metallic alloys, we would suggest to compare bulk steel to thin film steel. The main reason for the choice of this material lies in the vast literature about thermal treatments on this class of alloy that could be used for comparison. Although heat treatments on many other ferrous and non-ferrous alloys (Cu-Al, Al-Zn, Ni-Cr, Fe-Si, etc) are also well studied, metallurgical data about carbon steel are by far more available and systematic, including diagrams like Temperature-Time-Transformation, Continuous-Cooling-Transformation and Time-temperature-precipitation for a high number of specific elemental compositions. The study of simple thermal treatments in Fe-C alloys in the shape of thin films compared to the same treatments on bulk alloys would
allow to determine the influence of the increased surface/volume ratio and the effects of the interfaces on the nucleation and growth of phases and microstructures. Quenching treatments could also be employed to study the martensitic transformation on thin film steels of adequate elemental composition. Our advice is to start studying gradient composition of Fe-C and only in a second moment adding one more degree of freedom to the system by including a third alloying element. The addition of Ni or Cr would allow to study the stabilization effect for the ferritic/austenitic phases and, including local electrochemical methods (microcapillary analysis), also the study of the corrosion properties of stainless steel compositions in the shape of thin film. The Fe-C alloy could be directly deposited by magnetron sputtering of a carbon steel target or produced by co-sputtering of Fe and C. The first method should be preferred in the case of studies with thickness gradient, although a certain optimization should be applied to produce films with the exact elemental composition (due to the fact that different sputtering and deposition rates could exists for Fe and C) while the second method could be interesting to deposit and study films with an elemental composition gradient.

5.3.4 Technological applications

The improved knowledge of the interaction between elemental composition, thickness and heat treatments in thin films is of great importance for many application fields such as actuation, sensing, energy and information storage. An example of technological application of the results coming from the
present work could be the realization of mechanically active surfaces which could be used in aerodynamics, optics or bio-mimetics. Such surfaces would have the property of changing their local curvature or roughness in a controlled way so to guide fluids or to change their reflective behavior or their friction coefficient or their wettability. The working principle of such surfaces lies in the engineering of their local mechanical properties by the application of thin film metallic alloys using patterning techniques (masking, photolitography) and/or localized thermal treatments (e.g. laser, joule effect). Alternated layers of actuating materials and mechanically stiff alloys would allow the surface to deform in a pre-defined, controlled way. To provide an example, we will describe the design of a bio-mimetic, active surface for tunable fluid dynamic behavior. The skin of marine animals (sharks, dolphins) and the wings of insects (butterflies, moths) with regularly patterned roughness have been object of detailed studies [3-5] trying to understand the influence of these microscopic features on the lift and on the drag experienced by the animal in relative motion to the surrounding fluid (air or water). The results of these works show that the effects of these microstructured surfaces are manyfold: increased lift in insect wings, reduction of drag in shark skin, self cleaning (Lotus effect). Although the effects of these features are measurable, their magnitude is far from being spectacular and, as pointed out by Bechert et al. [3], applications of bio-mimetic replicas of these surfaces on macroscopic objects (cars, airplanes, ships, submarines) is at the present time considered antieconomical.
Nevertheless, what it is true for macroscopic world is not necessarily true in the case of micro and nanosized devices, where surface/volume, and therefore surface/weight ratio is significantly increased. In the technological field of micro and nanosized vehicles, where energetic efficiency is a key factor [6], micro-structured surfaces could provide a considerable advantage in both performances and economicity of such devices. Simple micro-structured surfaces could be applied as a skin to swimming robots, while coupled with actuating materials, the micro-structured surfaces could be employed to produce active wings for the so called “flapping wing micro air vehicles”. A possible way to produce a simple active wing with a micro-structured surface would involve the deposition of two thin layers of metallic alloys over a thin, flexible substrate, e.g. polyimide (PI). The first layer should be used to shape the surface of the wing with the described aerodynamically functional roughness. This could be achieved by depositing a patterned layer (photolithography + magnetron sputtering) of a material with high stiffness, e.g. Ni-W alloy, on an in-plane pre-strained PI foil, with a procedure similar to the one described by Choi et al. [7]. Releasing the in-plane pre-strain, the foil should produce an array of wrinkles whose shape would be guided by the patterned material (Fig. 5.1). The second layer should be a uniform thin film of an intrinsically actuating material, such as Ni-Ti alloy, providing the motion capability to the system, as proven by Friend et al. [8]. In the case of the Ni-Ti based shape memory alloy, a crystallization step should be included, since this material is known to be found in an amorphous state after the PVD
deposition (the polyimide substrate was actually chosen due to its capability of resisting the thermal treatments usually employed in SMA crystallization processes). To allow the SMA to flap the wing, the device should be coated while pre-shaped in the resting state of the flapping action, called shape “A”. After the deposition of the active layer, the system should be mechanically shaped while it is in the SMA martensitic state to the final shape of its flapping action, called state “B”. Once triggered, e.g. by means of the joule effect generated by an electric current, the wing would then switch between the two shapes, mimicking the flapping of the wing of an insect.

Fig. 5.1 Schematic description of the surface micro-structuring in 3 steps. 1: pre-strain of the PI substrate, 2: patterning of the surface by means of photolithography and magnetron sputtering deposition of Ni-W alloy, 3: strain removal and formation of surface wrinkles, 4: substrate shaped in the shape “A” before the deposition of the active layer, 5: deposition of the SMA layer, heat treatment, cooling to martensitic state, 6: deformation of the SMA in the martensitic state into the shape “B”.

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5.4 Conclusion

Combinatorial techniques, a special XRD procedure and a novel high-vacuum quenching setup (especially developed for thin films) were used to study the influence of elemental composition, film thickness and heat treatment on the crystallization mode, texture, grain size and phase formation (and therefore on mechanical properties) of Ni-based metallic alloys in the shape of thin films. Qualitative correlations among these parameters were evidenced and in particular it was observed that film thickness and quenching rates have a strong influence on the microstructure, crystallography and phase composition of metallic alloys in sub-micrometric dimensions. This research showed that the additional degrees of freedom (reduced dimensions, vapour deposition techniques) characterizing thin film metallurgy compared to its macroscopic counterpart may open the door to extremely interesting advances in the engineering of metallic materials properties. It was shown that the existing technical data (e.g. binary phase diagrams, thermal treatment diagrams) for macroscopic alloys may be difficult to apply to thin film materials. We therefore suggested to further investigate differences and similarities between alloys of similar compositions in both macroscopic and micro-nanoscopic dimensions, especially for metallic systems where an extensive amount of technical data is readily available (steels, bronzes, brasses, light-alloys). The results of this work, although far from giving any final answer to the all the questions that inspired it, may provide useful hints and tools to those who will continue in this task.
5.5 References:


6 Curriculum Vitae

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