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Some considerations on TiNi-based thin films for MEMS applications

Yongqing Fu, [1,2] Hejun Du [1,2] Sam Zhang [1], Yanwei Gu [1]

[1] School of Mechanical and Production Engineering, Nanyang Technological University, Singapore 639798

[2] Advanced Materials for Micro and Nano Systems Programme, Singapore-MIT Alliance, 4 Engineering Drive 3, Singapore 117576

Fax: 65-67911859, e-mail: myqfu@ntu.edu.sg

TiNi thin films have attracted much attention in recent years in the field of micro-electro-mechanical system (MEMS) applications. In this paper, some critical issues and problems in the development of TiNi thin films were discussed, including preparation and characterization considerations, residual stress and adhesion, frequency improvement, fatigue and stability as well as functionally graded thin films.

Key words: Shape-memory; TiNi; Sputtering; Thin Films; MEMS,

1. INTRODUCTION

Shape memory alloys (SMAs) possess an array of desirable properties: high power to weight (or force to volume) ratio, thus the ability to recover large transformation stress and strain upon heating and cooling, peudoelasticity, high damping capacity, good chemical resistance and bio-compatibility. More recently, thin film SMA has been recognized as a promising and high performance material in the field of micro-electro-mechanical system (MEMS) applications, since it can be patterned with standard lithography techniques and fabricated in batch process [1-3]. The phase transformation in SMA thin film is accompanied by significant changes in the mechanical, physical, chemical, electrical and optical properties, such as yield stress, elastic modulus, hardness, damping, shape recovery, electrical resistivity, thermal conductivity, thermal expansion coefficient, surface roughness, vapor permeability and dielectric constant, etc. These changes can be fully made use of the design and fabrication of microsensors and microactuators. However, due to the lack of full understanding of the thin film SMAs together with the controlling of the deposition parameters, they have not received as much attention in the MEMS technology as other microactuator technologies. In this paper, recent advances and development for TiNi SMA thin films were discussed.

2. MEMS REQUIREMENT for TINI FILMS

Successful implementation of TiNi micro actuators requires a good understanding of the relationship among processing, microstructure and properties of TiNi films, which include: (1) Low-cost, reliable and MEMS-compatible deposition methods with precise control of film composition and quality; (2) Reliable and precise characterization technologies for various properties; (3) An appropriate post-deposition annealing or aging process compatible with MEMS process; (4) low residual stress to prevent deformation of MEMS structure; (5) High actuation speed and fast response with precise control of deformation and strain; (6) Good adhesion on substrate; (7) Durable and reliable shape memory effects; (8) Wide range choice of working temperatures; (9) Good resistance to surface wear and corrosion, biocompatible (in case of application in bio-MEMS); (10) Precise etching and patterning of TiNi film compatible with MEMS process and the possibility of nano-size TiNi structures and actuators; (11) Prediction and modeling of non-linear behavior of TiNi films as well as design and simulation of TiNi thin film microactuators

3. ADVANCES in TINI THIN FILM

3.1 Sputtering deposition and post-annealing

TiNi based films are typically prepared using sputtering method. Transformation temperatures, shape memory behaviors and superelasticity of the sputtered TiNi films are sensitive to metallurgical factors (alloy composition, contamination, thermo-mechanical treatment, annealing and aging process, etc.), sputtering conditions (co-sputtering with multi-targets, target power, gas pressure, target-to-substrate distance, deposition temperature, substrate bias, etc.), and the application conditions (loading conditions, ambient temperature and environment, heat dissipation, heating/cooling rate, strain rate, etc.) [4,5].

Precise control of Ti/Ni ratio in TiNi films is of essential importance. The intrinsic problems associated with sputtering of TiNi films include the difference in sputtering yields of Ti and Ni, geometrical composition uniformity over substrate and along cross-section thickness of the coating, as well as erosion and roughening of targets during sputtering. To combat these problems, co-sputtering of TiNi target with another Ti target, or using two separate single element (Ti and Ni) targets, or adding titanium plates on TiNi target are widely used. Substrate rotation, good configuration of target position and precise control of sputtering conditions are also helpful. Since contamination is a big problem to good mechanical properties of the sputtered TiNi films, it is important to limit the impurities, typically oxygen and carbon, to prevent the brittleness. For this reason, the purity of Ar gas and targets is essential, and the base vacuum of the main chamber should be as high as possible (usually lower than 10^{-7} Torr). Pre-sputtering cleaning of targets before deposition effectively removes the surface oxides on targets, thus constitutes one of the important steps in ensuring film purity. In order to deposit films without columnar structure (thus with good mechanical properties), a low processing pressure of Ar gas (0.5 to 5 mTorr) or application of bias voltage is essential.

Depending on processing conditions, TiNi films can be deposited at room temperature or at high temperatures. TiNi films sputtered at room temperature are usually amorphous, thus post-sputtering annealing (usually higher than 450°C) is a must. Martensite transformation and superelasticity of TiNi films are sensitive to post-annealing and/or aging temperature and duration. It is suggested that the lowest possible annealing or aging temperature be used in a bid to conserve thermal processing budgets and more importantly minimize the reactions between film and substrate. Long term post annealing and aging process should be avoided since it could trigger dramatic changes in film microstructure (i.e., precipitation), mechanical properties and shape memory effects. Films deposited at a relatively high temperature (about 400°C) is crystallized in-situ, thus there is no need for post-annealing. Films can also be deposited at relatively high temperatures (400 to 500°C) at initial sputtering to form crystallized phase, then using a relatively lower temperature (about 300°C) to maintain a crystalline growth during the later sputtering process. Films can also be deposited at a low temperature (about 300°C) to get partial crystallization, then annealed at a higher temperature (500°C) for a short time to promote further crystallization. Recently a localized laser annealing method was studied for TiNi films in our group, where only certain areas of the film are annealed by laser beam to exhibit shape memory effect, and the other non-annealed areas remain amorphous, thus acting as a pullback spring during cooling process.

3.2. Characterization of TiNi films

For freestanding TiNi films, conventional methods, such as differential scanning calorimetry (DSC), tensile tests (stress-strain curves) and X-ray diffraction (XRD) are quite applicable. The stress-strain responses of freestanding films are commonly evaluated using tensile tests. For MEMS applications, the TiNi films are usually deposited on Si or related other substrates. One of the important issues in characterization of the TiNi films for MEMS applications is how to correctly evaluate the shape memory effects and mechanical properties of the constrained thin films on substrates. For this purpose, curvature and electrical resistivity measurements (ER) are widely used. Some new methods based on MEMS testing, such as bulge testing, TiNi/Si diaphragm, cantilever bending or damping are more appropriate for microactuator applications, which are compatible with small dimensions and high sensitivities. Nano-indentation testing with changes of temperature could reveal the different elastic and plastic deformation behaviors of austenite and martensite, thus is also promising for characterization of superelasicity, phase transformation and mechanical properties of the constrained thin films. In our group, an AFM based in-situ testing method has recently been applied to characterize the phase transformation behavior of the constrained films. With the change of temperature, the surface roughness values change drastically when transforming between the marteniste and the austenite phases, thus clearly reveal the occurrence of phase transformation. The advantages of this method are its nondestructive nature and applicability to very small size films (down to nanometers).

There are usually some discrepancies in transformation temperatures obtained from different characterization methods. The possible reasons include [6]: (1) the intrinsic nature of testing method; (2) differences in testing conditions, for example, heating/cooling rate; (3) the phase transformation and mechanical behaviors of the constrained TiNi films could be different from those of free-standing films, due to substrate effect, residual stress, strain rate effect, stress gradient effect and temperature gradient effect; (4) non-uniformity of film composition over whole substrate and along cross-section thickness of coating.

In film characterization, there are still many important issues unresolved: (1) Nucleation and growth mechanisms of TiNi thin films and substrate effects; (2) Effects of precipitation, point defects and dislocations; (3) Grain size effect, nano-grain and nanocrystalline structure on shape memory effect and phase transformation. The refinement of grain size can strongly modify the structural and thermodynamic properties, thus the mechanical properties of shape memory alloys; (4) Film thickness effect; (5) Formation of film texture and its control, and the effects on shape memory effect; (6) Internal and external stress on the arrangement of martensite variants, stress induced martensite and its shape memory phenomenon, etc.. (7) Surface chemistry, surface adsorption and biocompatibility of TiNi films with small grain size.

3.3. Residual stress and stress evolution

Residual stress and stress evolution in the films could pose potential problems in applications, as it may influence not only adhesion between film and substrate, but also deformation of MEMS structure, mechanics and thermodynamics of transformation and superelasticity effects, etc. Large residual stress could lead to either film cracking or decohesion under tension, or film delamination and buckling under compression. Deposition conditions, post-deposition thermo-mechanical treatment and composition in TiNi films could have important consequences with respect to the development of residual stress [7]. For a film-substrate system, possible origins of stress in thin films can be divided into three groups, i.e., thermal stress, intrinsic stress and phase transformation stress. In crystalline TiNi films, large tensile stress is generated during heating due to the phase transformation from martensite to austenite, while during cooling, the martensitic transformation occurs and the tensile stress drops significantly from the formation and alignment of twins and shear-variant boundary motion, etc. The stress generation and relaxation behaviors upon phase transformation are significantly affected by film composition, deposition and/or annealing temperatures, which strongly control the formation and evolution of intrinsic stress, thermal stress and phase transformation behaviors. The difference in residual stress for films with different Ti contents can be attributed to the differences in phase transformation behavior, intrinsic stress in the films, and/or precipitates in the films.

In order to minimize the residual stress in TiNi films, it is necessary to [8,9]: (1) precisely control the Ti/Ni ratio; (2) deposit films at a possible lower pressure; (3) select a suitable deposition temperature or annealing temperature, with a compromise between thermal stress and intrinsic stress; (4) use some interlayers (with possible compressive stress) to reduce large tensile stress in some TiNi films; (5) perform post-annealing, ion beam post-modification, or in-situ ion beam modification during sputtering in order to reduce intrinsic stress, (6) select suitable substrate to reduce thermal stress.

3.4. Frequency response

Applications of micro-actuators require high frequency and fast response (narrow transformation hysteresis). One of the challenges for the successful application of TiNi films is effective reduction of hysteresis and increase in operating frequency. The response speed of TiNi microactuators is mainly limited by their cooling capacities. The binary TiNi alloy films have a large temperature hysteresis of about 30°C. The hysteresis could be slightly reduced by decreasing the cyclic temperature amplitude and/or increasing working stress. R-phase transformation usually has a very small temperature hysteresis, which is useful for MEMS applications. However, the problem is that the strain and stress (or force) generated are too small to be of many practical uses. Addition of Cu in TiNi films is effective in reducing the hysteresis. However, the transformation temperatures of TiNiCu films decrease slightly, and the transformation becomes weaker with the increase of Cu contents, in terms of recovery stress, maximum recovery strain and heat generation, etc [10]. Also the film becomes brittle when Cu content is higher than 10 at%.

Generally speaking, the constrained films have smaller hysteresis as compared with freestanding films, and the film with large compressive stress could have much smaller (even almost zero) hysteresis compared with films with large tensile [11]. Therefore, selection of a suitable substrate (with larger thermal expansion coefficient than TiNi film) could help generate large compressive stress, thus a smaller hysteresis. Another way is to use external heat sinks. TiNi based films can be deposited on a suitable substrate with good thermal conductivity, like Cu plate, thus significantly improving thermal dissipation and working frequency. However, this brings in more critical issues, such as integration and compatibility with MEMS batch process, residual stress and adhesion.

3.5. Adhesion and interfacial analysis

When TiNi films are deposited on Si substrate, there exist interfacial diffusion and chemical interactions at the interface whereby titanium and nickel silicides may form during high temperature deposition or post-deposition annealing. These interfacial reaction products could be complex, heterogeneous and metastable. Since the TiNi film thickness required in MEMS applications is usually less than a few microns, a relatively thin reaction layer could have significant adverse effect on adhesion and shape memory properties. In MEMS processes, there is a need for an electrically and thermally insulating or sacrificial layer. Thermally grown SiO_2 is often used as this sacrificial layer. However, the adhesion of TiNi film on SiO_2 layer (or on glass and polymer substrate) is poor owing to the formation of a thin intermixing layer and the formation of a fragile and brittle TiO_2 layer. In a significant deformation or during a complex interaction involving scratch, this layer is easily broken, thus peel off. Adhesion of TiNi film on other substrates (such as Si_3N_4, polysilicon, etc.) is important for its successful MEMS applications, but few studies have been done so far.

3.6. Performance degradation

Stability and fatigue have always been concerns in development of TiNi thin films for applications. Fatigue of TiNi films is referred to the non-durability and deterioration of the shape memory effect after millions of cycles. The performance degradation and fatigue of thin films are influenced by a complex combination of internal (alloy composition, lattice structure, precipitation, defects, film/substrate interface) and external parameters (thermo-mechanical treatment, applied maximum stress, stress and strain rate, the amplitude of temperature cycling frequency) after long term thermal-mechanical cycles. For freestanding films, there are some studies using tensile tests to characterize the fatigue problems. Results indicated that there need tens of cycles before the stability of shape memory effects. The studies on fatigue of the constrained TiNi films using the changes of recovery stress during cycling showed that the recovery stress of TiNi films from curvature measurement decreased dramatically in the first tens of cycles, and becomes stable after thousands of cycles. Transformation temperatures also changed dramatically during cycling. This reduction of the recovery stress is believed to result from the dislocation movement, grain boundary sliding, void formation, or partial de-bonding at the film/substrate interfaces, non-recoverable plastic deformation, changes in stress, etc.

3.7. TiNi based films with varied transformation temperatures

The working principle of TiNi microactuators renders them very sensitive to environment. The maximum transformation temperature of binary TiNi thin films is usually less than 100°C. However, a lot of MEMS applications require higher temperatures. Ternary system is the solution: adding a varying amount of a third element, such as Pd, Hf, Zr, Pt, Au, etc., into the binary alloys easily adjusts the transformation temperatures from 100°C to 600°C. TiNiPd and $TiNiH_f$ films are also effective in decreasing the temperature hysteresis, thus promising for quick movement at higher temperatures. The potential problem is that all these high temperature ternary thin films are high cost with poor shape memory effect and brittleness problems. Small amount of Pd or Pt addition could reduce martensite transformation temperatures rather than increase them. Slight increase in Ni content in film can dramatically decrease the phase transformation temperatures.

3.8. Functionally graded and composite TiNi based films

To further improve the properties of TiNi films, multi-layer, composite or functionally graded TiNi based films can be designed. The common one is through the gradual change in composition (Ti/Ni ratio), crystalline structures, transformation temperatures, and/or residual stress through film thickness. As the Ti or Ni content changes in the micron-thick film, the material properties could change from pseudo-elastic (similar to rubber) to shape memory. The seamless integration of pseudo-elastic with shape memory characteristics produces a two-way reversible actuation, because residual stress variations in thickness will enable biasing force to be built inside the thin film. These functionally graded TiNi films can be easily prepared by sputtering deposition with slightly changing the target powers during deposition. Another novel way is to vary the target temperature during sputtering, and the films produced by hot targets have compositions similar to that of the target while films produced from cold target are Ti deficient. The second type of functionally graded films involves new materials and functions other than TiNi films. Recently we explored the deposition of a functionally graded TiN/TiNi layer to fulfill this purpose. The presence of an adherent and hard TiN layer (300 nm) on TiNi film (3.5 μm) formed a good passivation layer (to eliminate the potential Ni release), and improved the overall hardness, load bearing capacity and tribological properties without sacrificing the shape memory effect of the TiNi film [12,13]. Other functionally graded or composite designs include the combination of TiNi films with piezoelectric, ferromagnetic, or magnetostrictive thin films to improve response time. However, the complexity of the fabrication processing, the interfacial diffusion and adhesion, and dynamic coupling of dissimilar components remain tough issues for these types of composite thin films. Some surface modification methods, such as irradiation of TiNi films by electrons, ions (Ar, N, He, Ni or O ions), laser beams, neutrals can be used (1) to modify the surface physical, mechanical, metallurgical, wear, corrosion and biological properties for application in hostile and wear environment; (2) to cause lattice damage and/or alter the phase transformation behaviors along thickness of film, forming novel two-way shape memory actuation. The problems of these surface treatments are high cost, possible surface or ion induced damage, amorphous phase formation, or degradation of shape memory effects. Surface oxidation of TiNi bulk materials have often been reported to prevent the Ni ion release and improve its biocompatibility, and it is possible to do the same process for TiNi films with the sacrifice of shape memory effect.

4. SUMARRY

Some important issues pertaining to the preparation of high performance shape memory TiNi films using sputtering methods and their MEMS applications were discussed in this paper. Successful application of TiNi thin films in MEMS requires consideration of the following issues: preparation and characterization, residual stress and adhesion, frequency improvement, fatigue and stability, patterning and modeling of behavior.

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