THERMAL STABILITY OF TI/NI MULTILAYER THIN FILMS

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Abstract

In this work, thermal stability and mechanical properties of Ti/Ni multilayer thin films were studied. The multilayer thin films were synthesised by alternately depositing Ti and Ni layers using magnetron sputtering. The thickness of constituent layers of Ti and Ni varied from 1.7 nm to 10 nm, and one coating was deposited by simultaneous sputtering of both targets. Single crystalline silicon was used as a substrate. The effects of thermal treatment on the mechanical properties were studied using nanoindentation and discussed in relation to microstructure evaluated by X-ray diffraction. Annealing was carried out under low-pressure conditions for 2 hours in the range of 100–800 °C.

Keywords: Ti/Ni, multilayers, magnetron sputtering, nanoindentation, annealing

1. INTRODUCTION

By continually increasing demands and needs of humankind, science and research have reached a state where standard monolithic materials are no longer sufficient. Thanks to this, materials with a complex and advanced structure are currently being studied intensively.

One of the new trends in the thin films synthesised by plasma deposition is controlling the properties of coatings, for example, by alternating layers of various materials at the nanoscale and achieve functions that none of the original components has. In this way, it is possible to create a multilayered thin film with the option to choose the thickness of constituent layers, the ratio of layers thicknesses, the number of constituent layers, etc [1,2].

Ti/Ni multilayered thin films are one of the complex structures with superior functional properties (e.g. electric, magnetic and optical). These multilayered systems can be used to form TiNi shape memory alloys (SMA) which exhibit two closely related properties: shape memory effect (SME) and superelasticity (SE). These effects are caused by the martensitic transformation from a simple cubic structure (austenitic, phase B2) to a monoclinic crystalline structure (martensite, phase B19'), whereas this phase transformation is reversible and instantaneous. The transformation can be achieved by annealing or by applying stress [3,4]. Thanks to the remarkable SE and SME effects, TiNi SMA can be found in a wide range of fields such as medical, aeronautic, electric, telecommunication or as sensors and actuators in MEMS [4-8].

In this work, annealing was chosen to ensure the transformation. In the case of this approach, the uniformity of layers thicknesses on the nanoscale is crucial [9]. Moreover, for applications in MEMS, it is necessary to produce TiNi thin films with a thickness of several μm. For these reasons, magnetron sputtering is one of the most common deposition techniques to synthesise multilayer thin films with low total thicknesses and adequate uniformity. For the fabrication of Ti/Ni multilayer films, a dual-head sputtering system with Ti and Ni targets can be utilised and periodically turned the power on and off ensures alternating nanolayers of pure Ti and Ni. Afterwards, this multilayered system can be converted into the TiNi alloy thin film through solid state amorphisation by using a heat treatment. A significant advantage of magnetron sputtering over other deposition techniques used for multilayer thin films as e-beam evaporation, pulsed laser deposition or accumulative roll bonding, is an option of easily scalable resulting structure of multilayer by choosing deposition properties [10].

In this work, we have been mainly focused on thermal stability and development of mechanical properties with annealing of Ti/Ni multilayers prepared by dual-head magnetron sputtering of Ti and Ni targets. Annealed thin films composed of nanolayers with different thicknesses underwent nanoindentation tests, and results were discussed in relation to microstructure obtained by X-ray diffraction.

1. EXPERIMENTAL

Ti/Ni multilayers were synthesised by dual-head magnetron sputtering in an argon atmosphere. To ensure multilayer structure, the power on titanium and nickel targets was periodically turned on and off depending on which layer was currently depositing. Single crystalline silicon was used as substrates and before the deposition they were etched by ion bombardment for 5 minutes. During the deposition, the negative floating potential was applied on a substrate holder and to achieve sufficient spatial homogeneity, the substrate was rotating. By deposition of one-layered coatings of Ti and Ni, their deposition rates were found to be 0.75 nm/s and 1.52 nm/s, respectively. The desired thickness of an individual layer h was programmed by the variation of deposition time. The deposition conditions as applied power on targets, deposition pressure and substrate rotation speed for each multilayer design are listed in **Table 1**. The first presented coating h = 0 nm is prepared by simultaneous sputtering of both targets and therefore does not exhibits multilayered microstructure.

Table 1 Summary of deposition conditions of all Ti/Ni multilayered coatings

h (nm)	Overall thickness (nm)	Power on Ti target (W)	Power on Ni target (W)	Deposition pressure (Pa)	Rotation (rpm)
0	500	350	350	0.30	3.0
1.7	1190	300	300	0.16	4.8
2.5	1000	300	300	0.16	4.8
5.0	1000	300	200	0.16	4.8
10	500	350	350	0.30	3.0

After the deposition, one sample from each layering underwent a series of annealing in thermal desorption spectroscopy chamber from 50 to 800 °C. For each annealing, the constant temperature was kept for 2 hours.

One of the analytical methods utilised to study the effect of annealing was the depth-sensing nanoindentation performed on Hysitron TI950 Triboindenter equipped with a Berkovich tip. To determine the indentation hardness H and the reduced elastic modulus E_r, nanoscale measuring head was used. This head allows measure in the load range from 50 nN up to 11 mN with a resolution of 1 nN. Several quasistatic tests with 20 segments of partial unloading were performed in load control regime. As it is shown in **Figure 1a)**, each segment consists of three parts: loading, hold and unloading, and each part lasted 2 seconds. The result of such a loading function can be load-displacement curve plotted in **Figure 1b)**, where every partial load segment can be evaluated according to the standard procedure proposed by Oliver and Pharr [11]. Thanks to that, the depth profile of hardness and modulus can be obtained by this approach. Example of such depth profiles are plotted in **Figure 1c)**. In this work, single measurement consists of 16 load-displacement curves whose depth profiles were averaged and standard deviations were calculated. Values of the hardness and the reduced elastic modulus in the smallest common depth (negligible substrate influence) were used to compare samples and annealing temperatures.

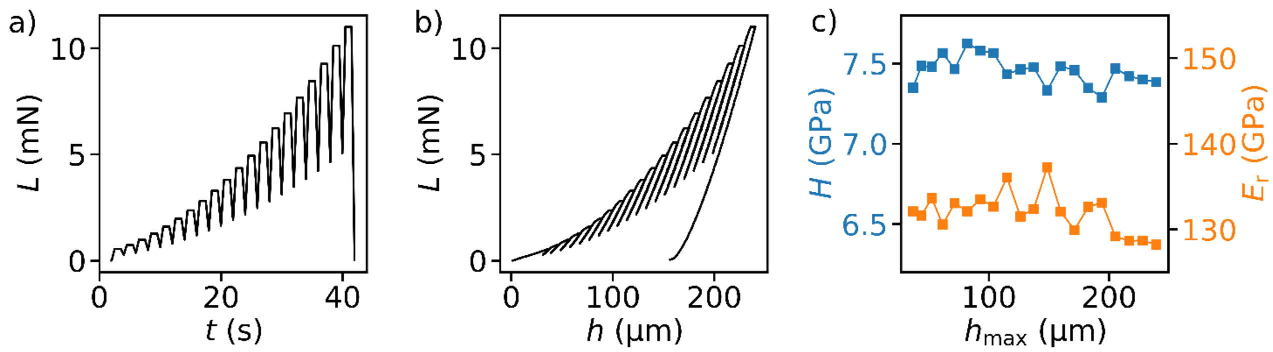

Figure 1 Quasistatic partial unload test: a) load function, b) load-displacement curve, c) hardness and reduced elastic modulus as a function of maximum depth per segment

In order to correlate the hardness and elastic modulus evolution with microstructural information, X-ray diffraction (XRD) was utilised for the phase identification. XRD experiments were performed in Rigaku Smartlab X-ray diffractometer using Cu Kα radiation with a wavelength of 0.15418 nm with a grazing angle of incidence configuration.

2. RESULTS AND DISCUSSION

The evolution of the hardness as a function of annealing temperature is plotted in **Figure 2** for each studied multilayer. The increase of hardness of as-deposited multilayers with the increasing layer thickness in the used range was already reported in our previous study [12] and interpreted as an interface crossing of single dislocations [13,14]. After the first set of annealing at 100 °C, differences between hardness values of coatings get smaller even almost equalised at 200 °C, what can be caused by alloying. With further increasing temperature, differences become more significant.

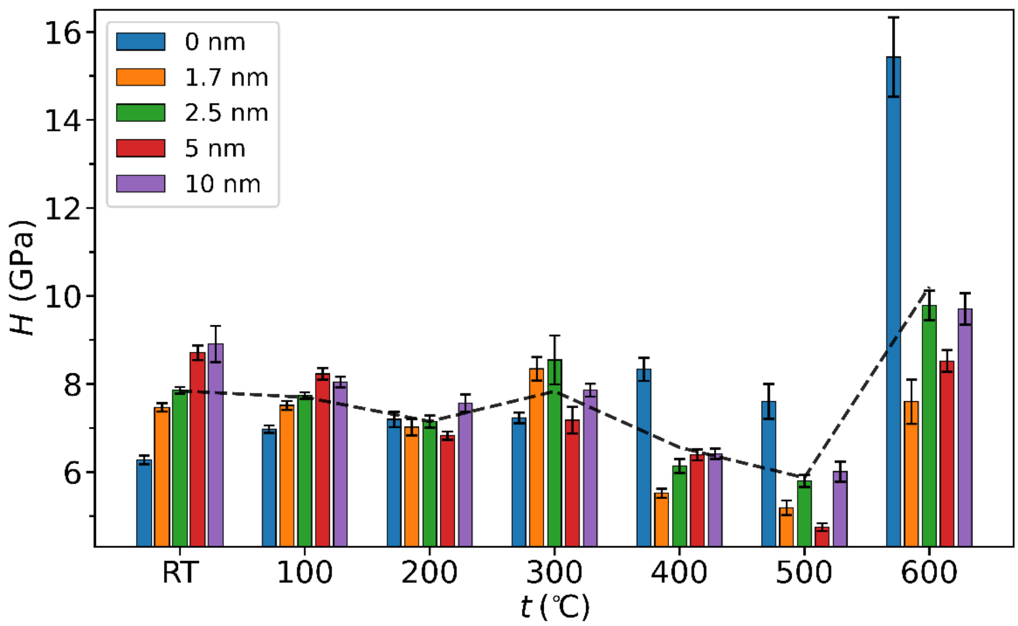

Figure 2 Development of hardness as a function of temperature for synthetised multilayers and one non-multilayer coating labelled as h = 0 nm

The average hardness for all coating and a specific temperature, marked by the dashed line, is continuously decreasing until 500 °C, except for annealing temperature 300 °C. At 600 °C hardness of multilayers significantly increased, and even more, a rapid increase occurred for non-multilayered coating (h = 0 nm) up to 15 GPa, which is more than twice as high as for the as-deposited coating. After annealing with even higher temperature, the coating has delaminated from the substrate or the coating has entirely desorbed. Substantial raise of hardness in the case of non-multilayer was not caused by higher substrate hardness, because the desorption was not observed even after annealing at 800 °C.

Reduced elastic modulus as a function of temperature was plotted in **Figure 3** in the same way as for hardness evaluation. From room temperature (RT) to annealing temperature 200 °C, order of reduced elastic modulus of multilayers was kept the same – maximum E_r for h = 5 nm and minimum E_r for h = 1.7 nm. Dashed line indicating reduced elastic modulus for all coating and the specific temperature has a very similar development as in the same graph plotted for hardness. The reduced elastic modulus is gradually decreasing until 500 °C, except for annealing temperature 300 °C, where the obtained value is slightly higher. After annealing at 600 °C, the reduced elastic modulus of multilayers increased but only a little. More significant influence of annealing temperature on the reduced elastic modulus was found in the case of multilayer with h = 1.7 nm. In this case the reduced elastic modulus decreased ~1.4 times at 500 °C in comparison with as-deposited multilayer. The significant influence of annealing was found for non-multilayer coating as well. In contrast to the as-deposited coating, after annealing to 600 °C, reduced elastic modulus increased ~1.3 times and was much higher than for multilayers.

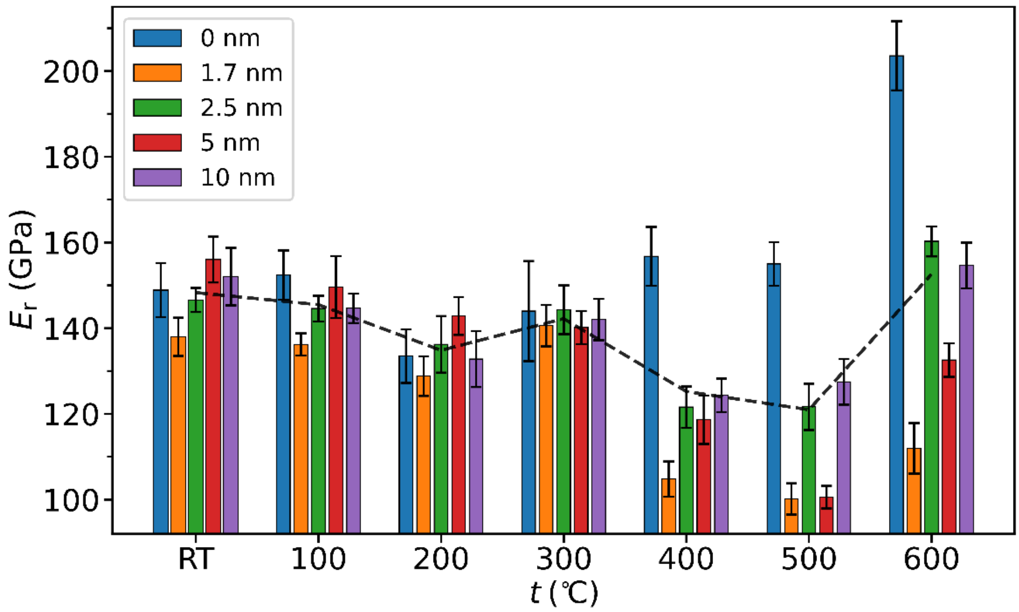

Figure 3 Development of reduced elastic modulus as a function of temperature for synthetised multilayers and one non-multilayer coating labelled as h = 0 nm

For both coatings where significant influence of annealing was found, XRD measurements were performed in the range RT–500 °C. The XRD diffractograms presented in **Figure 4a)** for h = 1.7 nm and in **Figure 4b)** for h = 0 nm exhibiting polycrystalline microstructure. The microstructure is composed of hexagonal (hcp) Ti, cubic (fcc) Ni grains and Ti-Ni intermetallic grains which emerged at higher annealing temperatures.

In the multilayer with h = 1.7 nm, Ni (111) stays as the strongest peak with increasing annealing temperature from room temperature until 300 °C. In this temperature range, the intensity of Ti (002) peak is decreasing, and this peak completely disappeared at 400 °C. Other notably lower peaks Ti (110), Ti (004) and Ni (222) disappeared as well. At this temperature, two new peaks corresponding to Ti-Ni intermetallic phase were detected, what is corroborated by previous works [15-17]. Shifted Ni (111) peak could contribute to the intensity of peak labelled as $TiNi_3$ (004). The disappearance of individual Ti and Ni peaks indicates possible disintegration of the layers and the formation of fully intermixed and alloyed structure. These phenomena can be the cause of a drop in hardness and reduced elastic modulus development. In the coating with non-multilayer structure, new intermetallic peaks did not emerge after higher annealing temperature, but they could contribute to the intensity of Ni (111) peak. This is highly probable due to a much easier way to form the alloyed structure from the non-multilayer structure. In this coating, noticeable shifting of the dominant peak is observed what can be caused by induced residual stress or by diffusion of atoms of one layer into another layer. Emerging and disappearing of Ti (010) and Ti (100) peaks is not clear yet, but more detailed investigations on this topic will be executed.

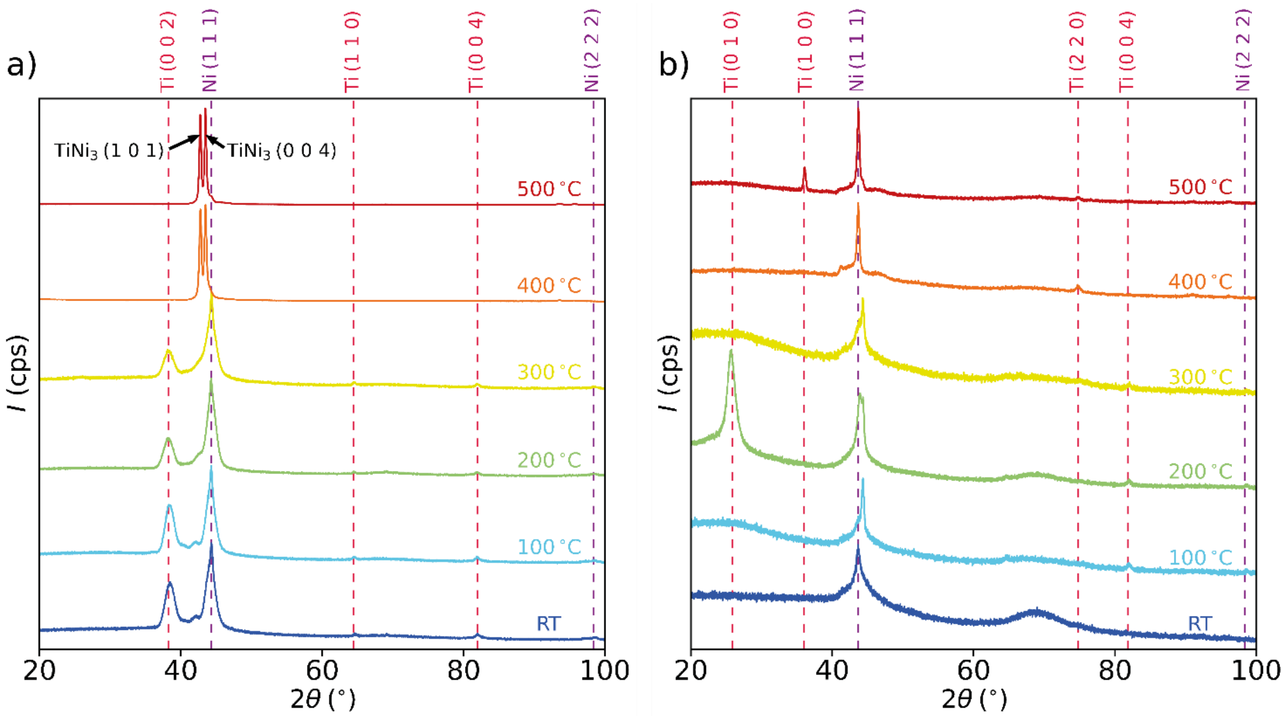

Figure 4 Diffraction patterns for Ti/Ni a) multilayer with individual layer thickness h = 1.7 nm, b) non-multilayer coating labelled as h = 0 nm

3. CONCLUSION

Several Ti/Ni multilayers synthesised by magnetron sputtering with different individual thicknesses of Ti and Ni layers were annealed. The main aim was to study the temperature dependence of their mechanical properties and to find a correlation with microstructural information. Based on the nanoindentation results, it was found out that hardness and reduced elastic modulus is decreasing with increasing annealing temperature until 500 °C. After annealing to 600 °C, both hardness and reduced elastic modulus increased especially in the non-multilayer coating (hardness of annealed at 600 °C is ~2.5x higher than for as-deposited). After annealing at even higher temperature, coating has delaminated from the substrate or entirely desorbed. From the XRD results, it was concluded that all synthesised coatings have polycrystalline microstructure, which is becoming intermix and alloy after annealing at ~400 °C. The XRD patterns were described, and different phenomena were explained, and correlation with mechanical properties was proposed.

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