Deposition of TiN layer on TiNi thin films to improve surface properties

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Abstract

TiNi based shape memory alloy (SMA) thin films have been widely used in biomedical and microelectromechanical systems. However, there are still some concerns for their wide applications because of their unsatisfactory mechanical and tribological performances, chemical resistance and biological reliability. This paper explored the deposition and effects of TiN protective layer on TiNi thin films to improve their surface properties while retaining the shape memory effects. Results indicated that the presence of an adherent and hard TiN layer (300 nm) on TiNi based SMA film (3.5 μm) formed a passivation layer, improved hardness and tribological properties, without sacrificing the phase transformation and shape memory effect of the TiNi film.

1. Introduction

TiNi based shape memory alloy (SMA) thin films offer a combination of novel properties, such as shape memory effect, pseudoelasticity, biocompatibility, deformation compatibility and high damping capacity, which enable them to be widely used in biomedical and microelectromechanical systems (MEMS) [1–9]. When TiNi based SMA thin films are applied in medical or MEMS devices, they must be able to fulfil functional requirements related not only to their mechanical properties, but also to their chemical and biological reliability. So far, there are still some concerns for the wide application of SMA bulk or thin films because of their unsatisfactory mechanical properties, chemical resistance and biological reliability.

High nickel content in TiNi alloys and potential nickel release often stimulate suspicions for their medical use [10,11]. Proper passivation to prevent surface layer degradation and nickel release into the environment was considered crucial for the medical applications of TiNi alloys. To apply TiNi surgical devices in the human body (such as orthodontic wires, cardiovascular and urological stents, bone fracture fixation plates and nails, etc.), the surface properties and corrosion resistance are important material characteristics. It was reported that TiNi exhibits poor resistance to localized corrosion in chloride containing environments, with low pitting potential values [12,13]. In addition, the healing of the passive film on TiNi was reported to be a slow and difficult process [14]. Therefore, a stable and corrosion-resistant passive layer is needed.

The good wear resistance is an important property for some biomedical applications such as medical guidewires, artificial bone joints, etc. If TiNi films are used in MEMS based pumps, grippers, valves, etc., there are also requirements for their wear, fretting and/or erosion properties. Even though it was reported that TiNi alloys with B2 phase (austenite parent phase) exhibit excellent wear resistance (due to its rapid work hardening and pseudoelastic properties) [15–19], poor wear resistance of B19' (martensite) and high coefficient of friction for both B2 and B19' phases made them difficult to be used in orthodontic applications. In the case of SMA films, interfacial adhesion is another major concern for their tribological application.

So far, there are many studies on the surface and biocompatibility of TiNi bulk materials [20,21], and it is generally agreed that the presence of an adherent and stable TiO2 film on TiNi bulk alloy surface could be beneficial to its corrosion resistance and biocompatibility. However, this layer is too thin, fragile and easy to be removed. Ion implantation [22,23], gas nitriding [24–
and TiN coating [13,27] were employed to improve surface properties of bulk TiNi alloys. After the surface treatment, hardness, wear and/or corrosion resistances were all improved. However, there are few reports on the modification of surface properties for sputter-deposited TiNi films. This paper explored the deposition and effect of TiN protective layer on TiNi thin films.

2. Experimental

TiNi films of 3.5 μm in thickness were prepared on (1 0 0) silicon substrate by co-sputtering a Ti0.5 Ni0.5 target (RF power density of 8.8 W/cm²) and a Ti target (DC power density of 0.3 W/cm²). During deposition, silicon wafers was heated to 723 K. The Ti/Ni ratio in the film was determined as 50.2/49.8 by energy disperse X-ray spectroscopy. Following deposition of TiNi film, a layer of TiN was prepared by sputtering the Ti target (DC power density of 4.4 W/cm²) in Ar/N₂ (1/1) atmosphere for 30 min at 723 K. The argon pressure used was 2.3 mtorr. X-Ray photoelectron spectroscopy (XPS) analysis was performed on both TiN coated and uncoated TiNi film surface using a Kratos AXIS spectrometer with monochromatic Al Kα (1486.6 eV) X-ray radiation. Crystalline structures of the films were obtained by grazing incidence X-ray diffraction (GIXD) (Cu Kα 40 kV/30 mA) with different incident angles. The crystalline structure changes during martensite transformations was analyzed by a Philips PW3719 XRD at different temperatures from 303 to 423 K. Martensitic transformation temperatures of the free-standing films were determined using a differential scanning calorimeter (DSC) at a heating/cooling rate of 5 K/min over a temperature range of 223–423 K. Stress evolution during martensite transformation was
measured using a Tencor FLX-2908 laser system at a heating and cooling rate of 1.0 K/min. Hardness and elastic modulus of the films were characterized using a nano-indenteter at an indentation depth of 100 nm. Scratch tests were used to evaluate the adhesion strength and friction proprieties of both uncoated and TiN coated TiNi films. Tribological properties of TiNi films and TiN coated TiNi samples were assessed using a ball-on-disk tribometer under dry sliding conditions at room temperature. Alumina balls (with a diameter of 9.5 mm and a surface roughness better than $R_s=0.05$ mm) were used as the counterface materials under normal loads of
Fig. 5. DSC result of TiN coated TiNi film.

Fig. 6. Stress evolution as a function of temperature for TiNi film and TiN coated TiNi films.

Fig. 7. Scratch test results for TiN coated and uncoated TiNi films. (a) Friction-normal load curve and (b) coefficient of friction-normal load curve.

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Fig. 2a shows the elemental depth profiling of TiNi films obtained by sputtering the surface with Ar⁺ ions. On the film surface, the dominant signals are from C, O, Ti and Ni, and oxygen content is approximately 36.92 at.%, Ti 31.03 at.%, Ni 18.54 at.%, and C 13.51 at.%. Both titanium and nickel contents increase significantly in the first 10 nm, and then maintain a stable ratio of 1/1 afterwards. The contents of oxygen and carbon decrease significantly. Oxide layer is approximately 15–20 nm thick, whereas carbon diffusion layer is less than 5 nm thick. As soon as TiNi film exposed to the air, oxygen and carbon quickly adsorb on the surface because titanium has a high affinity for oxygen and carbon (chemisorb barrier energy (enthalpy) for Ti and Ni to react with oxygen at surface are 241 and 956 kJ/mol, respectively [21]). The reduction of Ni on the

3. Results and discussions

3.1. Film characterization

TiN coated TiNi film appears typically TiN golden yellow in color. Fig. 1 shows AFM surface morphology of a TiN coated TiNi surface. The coating surface shows many grains with an average size of 300–400 nm. The roughness value, \( R_s \), obtained from AFM analysis is approximately 30–40 nm. AFM analysis reveals that deposition of TiN layer on TiNi films does not change the surface morphology.

1 and 5 N. The tests were conducted in laboratory ambient (25 °C and relatively humidity of 65±3%) for a sliding distance of 300 m at a sliding speed of 0.2 m/s.
film surface appears to be the result of preferential oxidation of Ti.

The composition profile of TiN coated TiNi films is shown in Fig. 2. As expected, the surface of the sample is dominated by Ti and N elements (with C and O peaks due to surface adsorption). Surface of TiN coated TiNi films is nickel free. Nitrogen can be detected 350 nm deep inside film. Traces of Ni element can be only detected 150 nm below the surface. SEM cross-section observation also confirms that TiN layer is dense and 300 nm thick. It is thus expected that this TiN layer probably could prevent surface layer biodegradation and act as a nickel diffusion barrier.

3.2. Phase transformation behaviors

Fig. 3 shows GIXD analysis of the TiN coated TiNi films with different grazing angles. With an incident angle of 1°, only the TiN phase is observed. With increasing X-ray penetrating depth, the phases change gradually from TiN to a combination of TiN and TiNi. The TiNi film structure is dominated by martensite (B19') with small amount of R-phase as shown in Fig. 3. XRD analysis was also performed at different temperatures and the results are shown in Fig. 4. It reveals the existence of martensite and austenite as well as TiN phases at room temperature. With the increase of tem-
perature, the martensite gradually changes to austenite (cubic) phase during heating, and vice versa during cooling.

Fig. 5 shows the DSC results of TiN coated TiNi film. During heating, a one-stage transformation from martensite to austenite is observed. The austenite transition start temperature (As, 338 K) is well above room temperature. During cooling, a two-stage transformation is observed corresponding the transformations among austenite, R-phase and martensite. The transformation temperature from R-phase to martensite phase is around room temperature (298 K), which can support XRD results. The transformation temperatures obtained from DSC curve do not show apparent changes with the addition of TiN layer. Wu et al. [24,25] reported that the martensite transformation temperatures of bulk TiNi alloy decreased slightly due to the large constrained stress originating from the thick ion-nitrided compound layers (a few micrometers thick), and also the composition changes (Ni-rich layer formed). In this study, TiN layer is quite thin (~300 nm thick), so this effect on martensite transformation temperatures of TiNi film is not so insignificant.

The results of stress evolution as a function of temperature for uncoated and TiN coated TiNi films are shown in Fig. 6. The stress vs. temperature plot demonstrates a closed hysteresis loop, a typical plot showing shape memory effect. During heating, the stress increases significantly due to the phase transformation from martensite to austenite until the temperature reaches to austenite transition finish temperature (Af). With further increase of temperature, transformation completes and generation of thermal stress occurs with the stress values decreasing linearly. During cooling process, tensile thermal stress develops in TiNi films. When the temperature is just above martensite transition start temperature (Ms), the residual stress reaches its maximum value. Cooling below Ms, the martensitic transformation occurs and the tensile stress drops significantly due to the formation and alignment of twins, shear-variant boundary motion and stress-induction of low-symmetry phases, etc. [28]. The recovery stress, given by the difference between the maximum and minimum stress, is approximately 350 MPa. Compared with the results from untreated and TiN coated TiNi films, there is no much differences, except that the residual stress is slightly lower for TiN coated TiNi films, indicating TiN layer has a compressive stress.

3.3. Mechanical and tribological properties

Hardness and elastic modulus values measured on the bare TiNi film are 2.5 and 55 GPa, respectively. With the addition of the TiN layer, the hardness increases significantly to 9.3 GPa, and the elastic modulus to 132 GPa. Since the thickness of the TiN layer is approximately 300 nm while the penetrating depth during indentation is approximately 100 nm, therefore, the hardness and modulus values are composite value from both TiN layer and the underneath TiNi film.

Scratch testing can be used to evaluate the load bearing capacity and friction properties of coatings under both normal and tangential force. The load-friction curve of TiNi films shows a rapid increase and large variation in friction force as shown in Fig. 7a, indicating the load bearing capacity is quite poor. For the scratch test on TiN coated TiNi films, the load-friction curve show a linear increase at the beginning period, with an abrupt increase at a critical load, after which film spallation occurs. Fig. 7b shows the corresponding curves of coefficient of friction vs. normal load for different specimens. For the stylus scratching on TiNi film, the coefficient of friction is relatively high (~0.4 as shown in Fig. 7b). Examination on scratch track shown in Fig. 8a reveals severe ploughing and delamination. With the stylus scratching on the TiN coated TiNi film surface, the coefficient of friction is relatively low and stable (<0.3) before and even after adhesion failure as shown in Fig. 7b. Examination on the wear track before coating spallation shows that there is not much wear and only slight scratching lines on the wear track indicating a good wear resistance (Fig. 8b). The hard TiN layer can serve as a protective layer for improving load bearing capacity; effectively reducing the coefficient of friction thus providing good tribological behavior.

For the sliding wear tests results, under a low load of 1 N, the coefficient of friction of bare TiNi film is relatively high, or 0.3–0.4 as shown in Fig. 9. With deposition of a TiN layer, the coefficient of friction maintains at approximately 0.15 during the sliding process (c.f. Fig. 9). In the wear track of bare TiNi films,
spallation of films are observed (Fig. 10a). Though the wear resistance of TiNi film is reportedly good [10–13], the relatively high coefficient of friction could have caused adhesion failure and interfacial debonding of films during the wear process. In the case of the TiN coated TiNi films, the wear tracks show only some scratches (Fig. 10b) with no other wear damage, owing to the decrease in coefficient of friction and improvement in surface hardness. When the normal load increased to 5 N, both the bare TiNi films and the TiN coated specimens showed spallation due to their poor adhesion to Si substrate, but the coefficient of friction value for TiNi films is approximately 0.6–0.7, while for TiN coated TiNi film, it is approximately 0.4–0.5.

Preliminary results already show the load bearing capacity and tribological properties of TiNi film can be effectively improved by application of a thin, dense and hard TiN layer. The deposition of TiN and TiNi films can be performed in sequence without breaking vacuum, making the process viable for easy production. Further systematic studies are being preformed on corrosion resistance and biocompatibility of TiN coated TiNi films.

4. Conclusions

A hard and adherent TiN thin layer of approximately 300 nm was successfully deposited on TiNi film of 3.5 μm using magnetron sputtering system. The following points are emphasized:

1. GIXD profiles at different incident angle indicate that the thin TiN layer is physically resides on top of the TiNi film without noticeable phase disturbance to the underneath TiNi layer.

2. Both DSC and curvature methods confirm that addition of the TiN layer has no noticeable effect on the shape memory effect and martensite transformation.

3. Although the TiN layer is approximately 300 nm, the load bearing capacity, friction and wear resistance of the TiNi films have been effectively improved.

References