Polymerized hexamethyldisilazane coated on equiatomic TiNi shape memory alloy using DC-pulsed plasma assisted chemical vapor deposition

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Abstract

SiC:H organic-like thin films are deposited on Ti₅₀Ni₅₀ shape memory alloy by asymmetric bipolar DC-pulsed plasma assisted chemical vapor deposition (PACVD) in the gas mixture of hexamethyldisilazane (HMDSN) and Ar at room temperature. The deposition rate of the plasma-polymerized HMDSN (PPHMDSN) thin film is faster than that of RF process and the PPHMDSN thin films not only enhance the corrosion resistance but make the corrosion current density decay four orders. The surface morphology of the films is very smooth and uniform and the root mean square of surface roughness is in the range between 3 and 5 nm. The organic-like thin films containing peroxides or free radicals can be grafted with polymer acrylamide (AAm) which can improve the biocompatibility of TiNi shape memory alloy.

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1. Introduction

TiNi-based shape memory alloys (SMAs) have the excellent shape memory effect (SME), superelasticity and biocompatibility [1] and have been used as a functional material in a variety of industrial and medical applications such as the intracoronary stent [2], the ligaments' replacement [3], the shape memory microvalve to control drug delivery [4], the bone stamp and osteosynthesis devices [5], etc. The biocompatibility of metal implants is generally evaluated by the reaction between metal and the surrounding tissue. The intensity of the damage caused by metallosis is proportional to the quantity of toxic metallic ions produced by corrosion. In TiNi-based SMAs, titanium is not detrimental among the essential trace elements [6], while nickel proves to exhibit high carcinogenic and toxic potencies *in vivo* regardless the fact that Ni is an essential element to the human body [7]. Hence, the passivity current density of the implanted metal in a potentiostatic condition can be taken as an index of the ion release of the metal and this current density is sufficient to be an indicator of its biocompatibility. Since the

corrosion resistance depends on the surface properties of the alloy, the coatings of plasma-polymerized hexamethyldisilazane (PPHMDSN) are employed in this study to improve the corrosion of Ti₅₀Ni₅₀ SMA and also to prevent the Ni ions releasing from Ti₅₀Ni₅₀ alloy. At the same time, the wettability, the relative wet friction coefficient and the feasibility to graft with polymer to improve their biocompatibility of PPHMDSN coatings on Ti₅₀Ni₅₀ SMA are also studied and discussed.

2. Experimental procedure

2.1. Substrate preparation

The Ti₅₀Ni₅₀ SMA was prepared from titanium (99.8 wt.%) and nickel (99.98 wt.%) by using a vacuum/argon tungsten arc furnace. The casting ingot was hot-rolled into 1-mm-thick sheet at 1123 K, and subsequently annealed for 30 min. The rolled sheet was cut into 10 × 10 × 1 mm specimens. The surface was ground on SiC papers to remove oxide and polished through a standard metallographic procedure to a final level of 1.0 μm alumina. Subsequently, all of the polished substrates were cleaned ultrasonically in cleaning reagents (Extran, MERCK Taiwan Ltd.), acetone and ethanol for 10 min to remove grease

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Fig. 1. Schematic diagram of the asymmetric bipolar DC-pulsed PACVD apparatus.

or organic contamination on the surface and then rinsed with de-ionized water, and finally air dried. These specimens were stored in a dried box before use.

2.2. Plasma-polymerized HMDSN on TiNi alloy

The substrate (Ti₅₀Ni₅₀ plate) was placed in the asymmetric bipolar DC-pulsed plasma assisted chemical vapor deposition (PACVD) equipment, as schematically shown in Fig. 1, and connected to a bipolar-pulsed power source [11] of high potential cathode. Plasma deposition was carried out under the given bipolar-pulsed source for 10, 20 and 30 min. The asymmetric bipolar-pulsed DC power is characterized by negative pulse voltage ($V = -800$ V) and reverse positive voltage ($V = +600$ V). The associated pulsed time of –on, –off, +on, and +off is 300 μ s, 10 μ s, 100 μ s and 10 μ s, respectively. Equivalently, frequency of the pulsed wave was 2.38 kHz.

The substrates were cleaned *in situ* prior to deposition by exposing the surface to argon (purity 99.9%) plasma for 3 min. Hexamethyldisilazane (HMDSN, (CH₃)₃SiNH₂Si(CH₃)₃, purity >98%, Mw = 161.40 g/mol, bp = 124–127 °C, $d = 0.774$ g/cm³, Fluka Chemical Co. Inc.) is degassed by a freeze–pump–thaw cycle before use. After the system is evacuated to a base pressure of 1.33 Pa or below, the gas mixed of HMDSN monomer vapor and argon was introduced into the chamber and adjusted to the work pressure of 33.33 Pa by the continuous monomer vapor flow. The HMDSN monomer has sufficient high vapor pressure at room temperature and, therefore, does not require any external warming. The film formed on the cathode has a highly cross-linked density.

2.3. Characterization of the deposited films

Film thickness is determined by the α -step method. The measured thickness value is the average of five readings. Static contact angle is measured by ERMA Goniometer (Model G1,

Erma Optical Works Co. Ltd., Japan) at room temperature, 26 °C, and five readings are averaged. Fourier transformation infrared (FTIR) spectra are obtained using a FTIR spectrophotometer (Model A202 Spectrometer, FT/IR-7000, Jasco, UK), to realize the functional groups formed after the glow discharge deposition. The spectra are obtained using a resolution of 4 cm^{–1} and are averaged over 40 scans.

Potentiodynamic polarization of the specimens is performed on AutoLab PGSTAT30 potentiostat in 278C Ringer's solution (Sintong Chem. Industry Co. Ltd., Taiwan). The composition of Ringer's solution is NaCl 8.6 g/l, KCl 0.3 g/l and CaCl₂·2H₂O 0.33 g/l. The working electrode is a specimen and the potential is imposed on the working electrode vs. the reference electrode (Ag/AgCl electrode). The applied voltage as well as the current flowing between the specimen and the platinum counter electrode is recorded automatically by data acquisition system. The voltage scanned toward the anodic direction until the breakdown potential is reached with the scanning rate of 300 mV per min.

Fig. 2. The figure of the deposition time vs. the thickness of thin film.

3. Results and discussion

3.1. FTIR characterization of the deposited films

The deposition rate of SiC:H organic-like (PPHMDSN) thin film deposited on TiNi alloy by asymmetric bipolar DC-pulsed PACVD of hexamethyldisilazane (HMDSN) and Ar gas mixtures is about 284.34 Å/min, as shown in Fig. 2. It is higher more than one order of the deposition process by RF-plasma PACVD, but slower than that by asymmetric bipolar DC-pulsed plasma PACVD [8,9]. Fig. 3 shows the infrared (IR) spectra of PPHMDSN thin films of different deposition time. The IR spectra of HMDSN monomer, as shown in Fig. 3(a), are characterized by the asymmetric Si–N–Si stretching at 939 cm^{−1}, the Si–N bending at 1186 cm^{−1}, the Si–(CH₃)₃ stretching vibration at 850 cm^{−1}, the Si–CH₃ rocking at 1258 cm^{−1}, and the stretching vibrations of methyl groups around 2960 cm^{−1}, 2923 cm^{−1} and 2853 cm^{−1} [10–12]. In contrast to the spectra of PHMDSN film shown in Fig. 3(b)–(d), these absorption intensities of the methyl group obviously increase with increasing the deposition time. In the range of 1200–3000 cm^{−1}, the three most conspicuous characteristic absorption peaks related to H bonds around 1250–1260 cm^{−1}, 2130 cm^{−1} and 2960 cm^{−1} are assigned to the symmetric stretching of Si–CH₃, Si–H and –CH₃, respectively. The other absorption peaks are characterized by Si–N stretching at 930 cm^{−1}, Si–CH₃ rocking–stretching at 840 cm^{−1} and Si–C stretching at 790–800 cm^{−1} [12–14]. HMDSN monomer contains no oxygen. However, there is Si–O stretching vibration peak at 1020 cm^{−1}. The oxygen in the deposited film may come either from the moisture of the chamber or from the trace impurity in the monomer and argon gas. The related absorption peaks shown in Fig. 3 are listed in Table 1 [15]. The IR spectra show that the origin Si–NH–Si bonds are destroyed

Table 1

The chemical bonds and their related absorption peaks of (a) HMDSN monomer and (b) PPHMDSN thin films shown in Fig. 3

(a)	
Chemical bonds	Absorption peak (cm ^{−1})
N–H	3350
Si–N	900
Si–(CH ₃) ₁	1260, 794
Si–(CH ₃) ₂	1260, 794
Si–(CH ₃) ₃	1260, 794, 855
Si–(CH ₃) _x	1260
Si–C	790
–CH ₃	2960
–CH ₂	2900
(b)	
Chemical bonds	Absorption peak/cm ^{−1}
Si–C	790
Si–(CH ₃) _x	840, 1260
Si–N	939
Si–O	1020
Si–H	2130
–CH ₃	2960
N–H	3350

by the plasma and formed new bonds, Si–H, which do not exist in the origin HMDSN monomer.

The $\equiv\text{Si}-\text{CH}_3$ will be bombarded by free radical or other high energy particle and dissociated to other structure as following:

or

The products of the above equations will react with each other and form silane and methane gas to diffuse out [12,16].

3.2. Surface property of the deposited films

Fig. 4(a) shows the cathodic and anodic polarization Tafel curves for the virgin TiNi substrate. The flat portion of the curve, known as the passive region, indicates that the TiNi readily forms a passive film. The open circuit potential (OCP) and the corrosion rate are approximately 0.3740 V and 0.5696 μA/cm², respectively. However, the reproducibility of the breakdown (pitting) potential for the as-homogenized TiNi is poor and ranges from 0.712 eV to 1.299 eV and gives widely scattered results, as reported in many studies [17–20]. For the PPHMDSN coatings with different deposition time, as shown in Fig. 4(b)–(d), the improvement of corrosion resistance is very remarkable. The fluctuation at the voltage below the breakdown potential is associated with the electrical noise due to the

Fig. 3. The IR spectra of (a) the HMDSN monomer, and the PPHMDSN thin films of different deposition time: (b) 10 min, (c) 20 min and (d) 30 min.

Fig. 4. The cathodic and anodic polarization Tafel curves for the thin films: (a) TiNi substrate, (b) 10 min, (c) 20 min and (d) 30 min.

resolution limitation of the potentiostat. The PPHMDSN film on TiNi can reduce the current density by at least four orders of magnitude. At the same time, the outstanding improvement shown in Fig. 4(b)–(d) may be attributed to the higher resistance and the more homogeneity (pinhole-free) of the deposited film. The hydrophobic and pinhole-free properties will prevent the TiNi from water uptake, leading to lower ionic conduction by many orders of magnitude. The higher thickness of the PHMDSN film may also account for the substantial improvement.

The wettability of the deposited films can be evaluated from the water contact angle of specimens. The material hydrophilicity is determined by its chemical structure. The stronger the polarity of the functional groups, the better the affinity with water. The water contact angle of as-polished TiNi alloy is 42° , as indicated in Fig. 5(a). After PPHMDSN deposition, the water contact angle raises from 42° to 87° , as shown in Fig. 5(b), because the PPHMDSN film consists of more non-polar groups as methyl and methylene.

The other index for evaluating the slippery surface is the wet friction test. Samples with different applied loads were moved onto the wet glass. The lateral force and displacement are

measured. The relative wet friction coefficient can be determined from the slope of the linear relationship between the maximum lateral force and the applied load, as the example of deposited PPHMDSN thin film shown in Fig. 6. The relative wet friction coefficient of TiNi alloy is about 0.2217. After deposition of PPHMDSN thin film, the surface becomes more hydrophobic, leading to the increase of relative wet friction coefficient, say, 0.2539. Fig. 7 shows the atomic force microscope (AFM, NT-MDT Solver P47) 3D image of PPHMDSN thin films deposited by different time. Under all the experimental conditions, the root mean square of surface roughness of the deposited PPHMDSN thin films measured by AFM is in the range between 3 and 5 nm (the as-polished roughness is 2.6 nm).

3.3. Possible uses of biocompatibility improvement of the deposited films

In this study, SiC:H organic-like thin films are deposited on TiNi SMA by asymmetric bipolar DC-pulsed PACVD of HMDSN and Ar gas mixtures at room temperature. However, their hydrophobic surface is disadvantage to medical application. The IR spectra show that the deposited PPHMDSN thin films

Fig. 5. The water contact angle: (a) measure method, (b) TiNi substrate, and (c) PPHMDSN thin film.

containing peroxides or free radicals can be subsequently grafted with hydrophilic polymer acrylamide (AAm) by UV-induced grafting polymerization [21]. The AAm grafting can be verified from the presence of amide group according to the IR spectra. The slippery property of the coated AAm is beneficial to the biomedical application of TiNi SMAs [21]. For example, heparin can be

Fig. 6. The wet friction test of the PPHMDSN thin film: the applied load vs. the maximum lateral force.

Fig. 7. The AFM 3D image of the PPHMDSN thin films of different deposition time: (a) 10 min, (b) 20 min and (c) 30 min.

immobilized onto grafted-AAm thin films to take TiNi SMA into the anti-thrombin biomaterials.

4. Conclusions

SiC:H organic-like thin films are deposited on TiNi shape memory alloys (SMAs) by asymmetric bipolar DC-pulsed

plasma assisted chemical vapor deposition (PACVD) of HMDSN and Ar gas mixtures at room temperature. The deposition rate of the plasma-polymerized HMDSN (PPHMDSN) thin films is faster than that of RF process and the root mean square of surface roughness is in the range between 3 and 5 nm. The PPHMDSN thin films not only enhance the corrosion resistance but make the corrosion current density decay four orders. Based on the micro-FTIR spectra, the Si–C and C–H bonds of the original HMDSN monomer are broken and new Si–H and C=O bonds are formed. The free radicals react with each other and form silane and methane gas which will diffuse out. After deposition of PPHMDSN thin films, the water contact angle will raise from 42° to 87° because the PPHMDSN film consists of more non-polar groups as methyl and methylene. The surface becomes more hydrophobic, leading to the increase of relative wet friction coefficient. The organic-like thin films containing peroxides or free radicals can be grafted with polymer to improve the biocompatibility of TiNi shape memory alloys.

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