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Development of Physical Vapor Deposition Technique and Testing on Ceramics and CoCrMo Alloys

Feng-Min Lai[1]* and Tan-Chih Chang[2]

[1]Department of Medical Engineering,
Da-Yeh University, No. 168, University Rd., Dacun, Changhua, Taiwan (R.O.C.)
[2]Department of Mechanical and Automation Engineering,
Da-Yeh University, No. 168, University Rd., Dacun, Changhua, Taiwan (R.O.C.)

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In this study, TiN thin films were coated on CoCrMo alloys and ceramic samples using vacuum coating technology with high-power impulse magnetron sputtering (HiPIMS), which was followed by coating at 100 and 200 °C to a thickness of 250, 500 or 750 nm to enhance the characteristics of the coated alloys. Through X-ray diffraction measurements, scanning electron microscopy, and microscale hardness testing, the structural, morphological, and mechanical characteristics of the CoCrMo and ceramic samples coated with TiN films were investigated in detail. The experimental results revealed that a smooth surface can be achieved on the film of 250 nm thickness and indicated that the TiN film with the smoother surface, formed by the vacuum coating method, has a higher hardness. It was also found that the TiN film prepared by coating at 200 °C had the smoothest surface and the highest hardness (365.64 HV0.5), leading to enhanced mechanical properties of the CoCrMo alloys. In the ceramic samples, the TiN film prepared by coating at 100 °C had the smoothest surface and the highest hardness (376.81 HV0.5). In addition, the vacuum coating process is helpful for improving the mechanical properties of TiN coating. The TiN materials are used in many sensor applications, and sensor applications can be realized using TiN/CoCrMo materials. In the future, we will study the sensing performance of TiN sensors fabricated on CoCrMo alloys, as well as implants made using the coated alloys. Then, we will further study circuit substrates, heat-resistant sensors, and corrosion- and wear-resistant parts that can be applied with TiN/Al_2O_3 materials.

1. Introduction

In recent years, Al_2O_3 ceramics have been used in circuit substrates, heat-resistant sensors, and corrosion-resistant parts, and CoCrMo alloys have been widely used in medical implant applications including the replacements of human joints and dental treatments.(1–3) This is because of the many advantages of Al_2O_3 ceramics and CoCrMo alloys, including good mechanical properties, excellent wear resistance, and superior corrosion resistance. The high biocompatibility of CoCrMo alloys with the human body is correlated to their superior corrosion

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*Corresponding author: e-mail: fengmin@mail.dyu.edu.tw
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resistance. However, when CoCrMo alloys are immersed in various solutions and biological environments, the Co element is easily dissolved. This will result in the instability of the oxide film in the human body. Despite the many advantages of CoCrMo alloys given above, the release of metal elements from orthopedic implants into body fluids is unavoidable. Then, such elements migrate through the tissue, which is very detrimental to the human body. To overcome these disadvantages of applying CoCrMo materials in implants, it is advantageous to coat them with a TiN film. Many ceramic films, including TiN and TiC, have been deposited on the surfaces of CoCrMo alloys.(4,5) TiN coating exhibits excellent chemical stability and high hardness, resulting in good protective properties.

The surface mechanical properties of n-Al_2O_3/Ni composite or Zr–O coating were improved when Ni and ZrO films were deposited on Al_2O_3 ceramics by Xu *et al.*(6) Zhitomirsky *et al.*(7) investigated Zr–O/Al–O coating, as well as bulk ZrO_2 and Al_2O_3 reference samples, using X-ray photoelectron spectroscopy (XPS). Li *et al.*(8) studied TiN films, which showed good toughness, and Al_2O_3/TiN multilayer materials with reduced coefficients of friction by modulated pulsed power magnetron sputtering, and Oh *et al.*(9) investigated the characteristics of Al_2O_3/ZrO_2 laminated films grown by ozone (O_3)-based atomic layer deposition (ALD) at low temperatures, in the form of thin-film encapsulation (TFE). Tkadletz *et al.*(10) exploited the full potential of wear-resistant hard coatings and introduced a portfolio of characterization techniques that enable the determination of complementary microstructural and mechanical properties of wear-resistant hard coatings.

In this paper, we describe physical vapor deposition (PVD) coating technology, as well as the deposition parameters suitable for providing hard TiN film coatings on Al_2O_3 and CoCrMo alloys. To explore the hardness of TiN films, test samples were subjected to a pretreatment of high-power impulse magnetron sputtering (HiPIMS). The HiPIMS technology is often used in medical, aerospace, electronics, sensors, and optoelectronic industries, and can increase the precision and merit of products. There are many different surface coating technologies, including electroplating, hot dip coating, chemical vapor deposition, and physical vapor deposition (PVD). The highest density and smoothness of TiN films are determined when using the HiPIMS technology, which is a PVD method. However, various industries also employ surface coating technology, which includes vacuum coating TiN technology used for implants and biomedical material coating technology. The enhanced mechanical strength, thermal stability, wear resistance, corrosion resistance, chemical stability, and high hardness of ZrO have been studied by Reeswinkel *et al.*(11), and Kumar *et al.*(12) reported that the density and smoothness of TiN films treated with HiPIMS coating technology increased with process temperature. Godoy-Gallardo *et al.*'s(13) study of antibacterial coatings may significantly affect the progress of the understanding of peri-implantitis and the cause of bone loss in animal experimentation. According to the literature, earlier work by Shukla *et al.* on the nitriding of CoCrMo alloy utilizing the novel HiPIMS discharge showed that this technique can be successfully applied to improve the wear resistance of the base alloy,(14) and Elmkhah *et al.*(15) studied HiPIMS-TiN coatings, which have a well-defined dense noncrystalline structure and not only are smoother but also have superior passivation and better protect the substrate against the ingress of aggressive anions than the substrate itself.

In this study, TiN films were grown on CoCrMo and ceramic substrates by the HIPIMS technique to obtain the highest density and smooth TiN films on these substrates. Their characteristics including hardness, surface features, and crystal structure were all analyzed. As mentioned above, ceramic and CoCrMo materials are used for numerous sensor applications. The results obtained in this study indicate that the desired characteristics of TiN films deposited on ceramic substrates and CoCrMo alloys can be realized. In the future, we will further study the sensing performance of TiN film sensors fabricated on Al_2O_3 ceramics and CoCrMo alloys, which are characterized by their surface smoothness and hardness. Implant and sensing applications can be realized with TiN/CoCrMo materials. Then, we will further study circuit substrates, heat-resistant sensors, and corrosion- and wear-resistant parts that can be fabricated using TiN/Al_2O_3 materials.

2. Experimental Procedure

In this study, the coating on a porcelain tooth was deposited using HiPIMS coating technology. The substrates employed for the TiN coating were Al_2O_3 ceramic and CoCrMo (ASTM F1537, ASTM F799) standard forging materials for surgical implants. Before the TiN coating process, the samples were ultrasonically cleaned in acetone and isopropyl alcohol to remove organics and other impurities.

In the experimental processes, first, the coatings were deposited on both Al_2O_3 ceramic and CoCrMo substrates using a TiN target to obtain the best process parameters; substrates were used for characterizing the mechanical properties. Second, the samples were subjected to evenness and hardness tests to analyze the mechanical properties. Finally, two substrates were used for determining the coating thickness and optimal process parameters for both substrates. The experimental method used is shown in Fig. 1.

The crystal structures of the TiN-coated ceramic and Co-Cr-Mo samples were determined by X-ray diffraction (XRD) (PANalytical, X'Pert Pro MRD). The surface morphologies of the samples were observed by scanning electron microscopy (SEM) (S-3000H, Hitachi). The hardness of the samples, defined as the resistance offered by the material to indentation, i.e., to permanent deformation and cracking, was analyzed using a Vickers microhardness test machine.

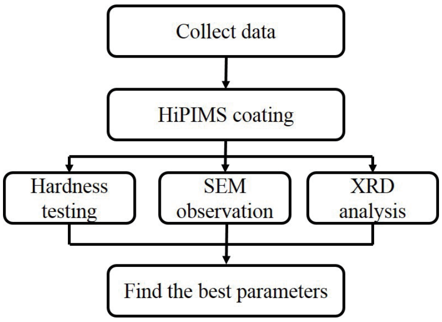


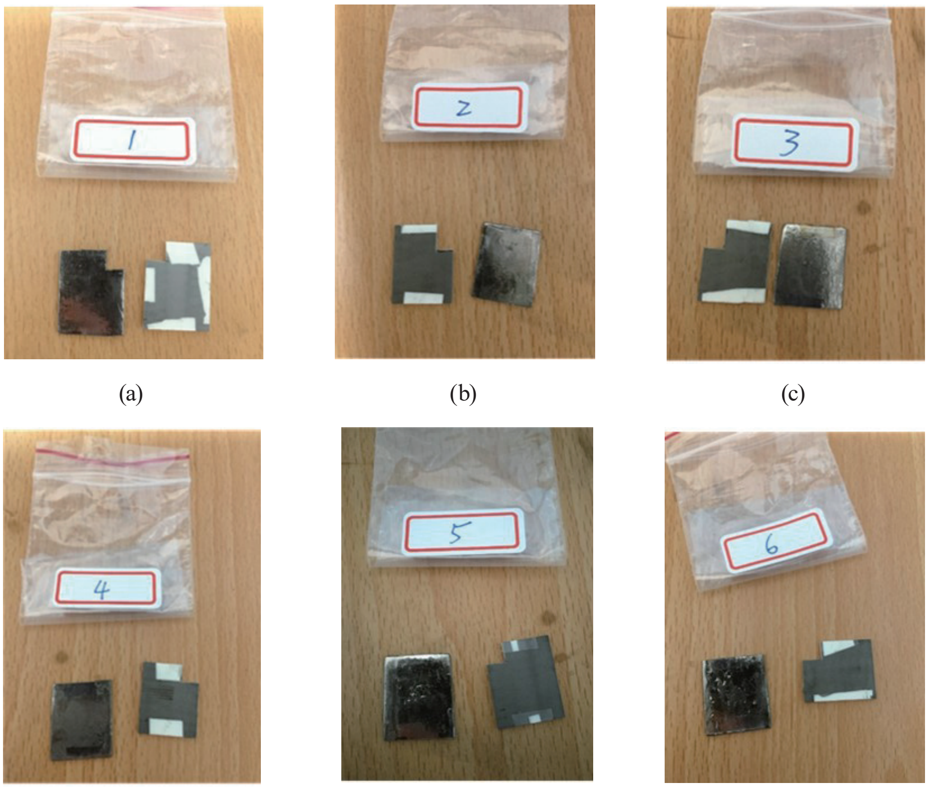
Fig. 1. Experimental method used.

2.1 Preceding operation and process parameters of HIPIMS

The substrates were cut into small samples of 1 × 1 cm^2 size before coating. The samples were degreased and cleaned in an ultrasonic cleaner to introduce them to the deposition chamber. Then, the depositions of HiPIMS coatings were performed using the TiN target on the base samples with the average power kept constant at 600 W for all depositions. Moreover, the pulse on/off times of 45 µs/955 µs and the growth pressure of 0.02 Torr were used for film growth. The Ar and N_2 gas flow rates were maintained at 30 and 5 sccm, respectively. The substrate temperature and film thicknesses are shown in Table 1. The photographs of these coated samples are shown in Fig. 2.

Table 1
Substrate temperatures and thicknesses of HiPIMS-TiN films on CoCrMo and ceramic substrates.

Values	Group					
	1st group	2nd group	3rd group	4th group	5th group	6th group
Temperature (°C)	100	200	100	200	100	200
Film thickness (nm)	250	250	500	500	750	750



(a) (b) (c)
(d) (e) (f)

Fig. 2. (Color online) Coated samples of (a) 1st, (b) 2nd, (c) 3rd, (d) 4th, (e) 5th, and (f) 6th groups.

2.2 Vickers hardness test

The Vickers hardness test of the coating samples was performed using the hardness tester for the surface hardness. Three scratches were run per sample with the force increasing to 70 N and the testing time of 15 s.

2.3 SEM observations of sample surface after coating

The coated-sample surface was observed by SEM at 5000×, 10000×, and 20000× magnifications.

2.4 X-ray diffraction (XRD)

The crystal structures of the HIPIMS-TiN-coated ceramic and Co-Cr-Mo samples were determined by XRD (PANalytical, X'Pert Pro MRD). In the XRD measurement, the Cu Kα line (λ = 1.541874 Å) was employed as the source and Ge (220) was adopted as the monochromator.

3. Results and Discussion

3.1 Hardness of HiPIMS coating

In this study, the coating samples were analyzed in terms of the hardness of TiN films deposited on two substrates, as shown in Fig. 3. It is known from the experimental results that the TiN film is deposited on the CoCrMo substrate. When the substrate temperature is 100 °C, the thickness of the deposited TiN film can reach 250 nm, and the highest hardness can be 365.64 HV. On the other hand, as shown in Fig. 4, on the ceramic substrate, the 250-nm-thick TiN film grown at the substrate temperature of 200 °C exhibits the highest hardness of 376.81 HV. The hardness values of TiN films deposited on CoCrMo and ceramic substrates at 100 and 200 °C are shown in Table 2. The difference in the hardness of TiN on CoCrMo substrates was

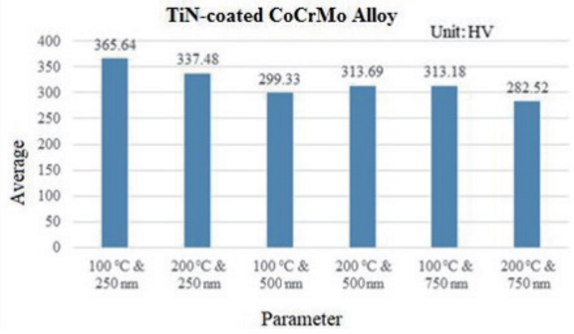


Fig. 3. (Color online) Hardness test results for CoCrMo samples.

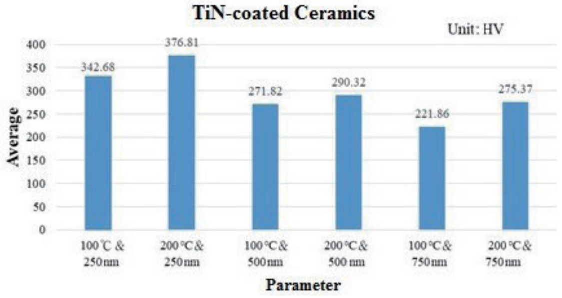


Fig. 4. (Color online) Hardness test results for ceramic samples.

Table 2
Hardness values of coatings.

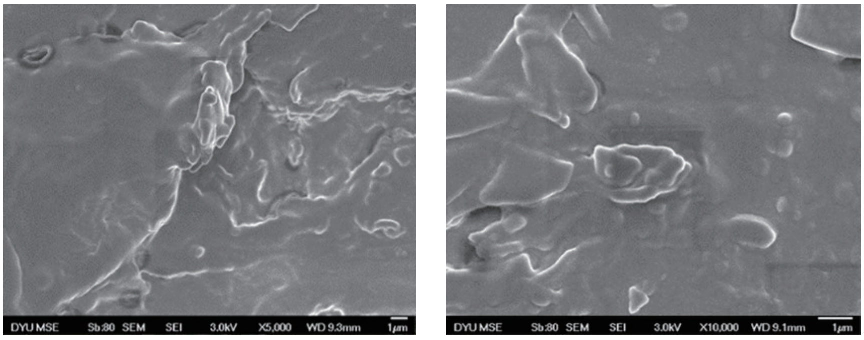
Hardness	Coating					
	100 °C/ 250 nm	200 °C/ 250 nm	100 °C/ 750 nm	200 °C/ 750 nm	100 °C Differential Values (%)	200 °C Differential Values (%)
Coating on CoCrMo	365.64	337.48	313.18	182.58	16.7	42.4
Coating on ceramics	342.68	376.81	221.86	275.37	35.3	29.6

Differential Values (%) = $(Hv_{max} - Hv_{min}) \times 100\% / Hv_{min}$

determined to be 16.7% at the substrate temperate of 100 °C and 42.4% at 200 °C. The difference in the hardness of TiN on ceramic substrates was determined to be 35.3% at the substrate temperature of 100 °C and 29.6% at 200 °C.

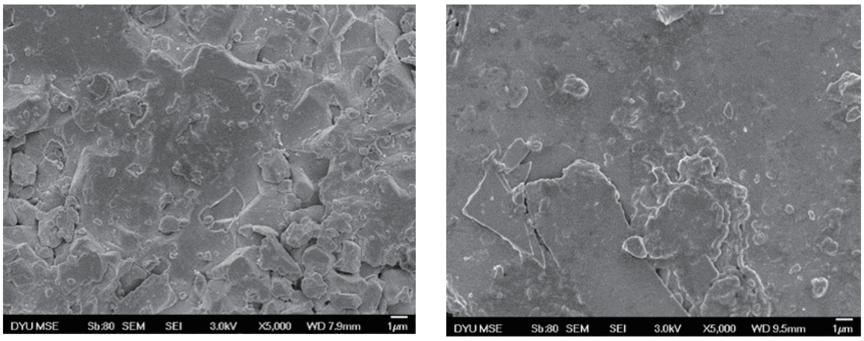
3.2 SEM observations of ceramics and CoCrMo samples with various HIPIMS coatings

From the hardness results, the optimum coating parameters for the TiN film on the CoCrMo substrate were obtained as the substrate temperature of 100 °C and the thickness of 250 nm. Additionally, the worst coating parameters for the film on the CoCrMo substrate were the substrate temperature of 200 °C and the thickness of 700 nm. On the other hand, for the TiN film deposited on the ceramic substrate, the optimum coating parameters were the substrate temperature of 200 °C and the thickness of 250 nm, whereas the worst growth conditions were the substrate temperature of 100 °C and the thickness of 250 nm. Figures 5–10 show the SEM images of the surfaces of these TiN-coated samples. We can see that the surfaces shown in the left figures are smoother than those in the right figures. A comparison of the surfaces obtained with the optimum and worst coating parameters reveals that the sample with a smoother surface had a higher hardness than that with a rougher surface.



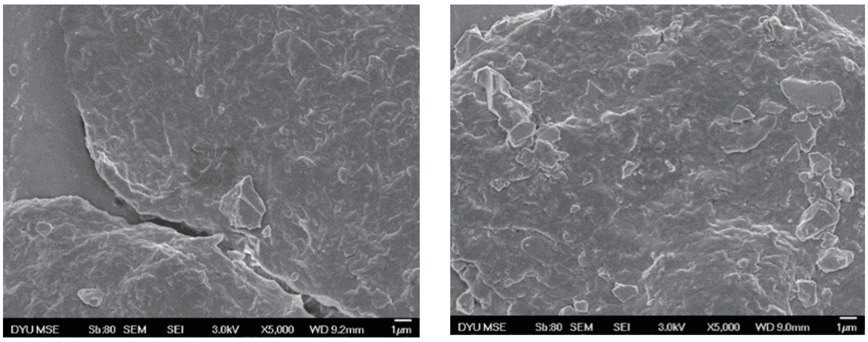
(a) (b)

Fig. 5. (Color online) TiN coating parameters on CoCrMo sample: (a) 100 ℃/250 nm and (b) 200 ℃/250 nm observed at 5000X.



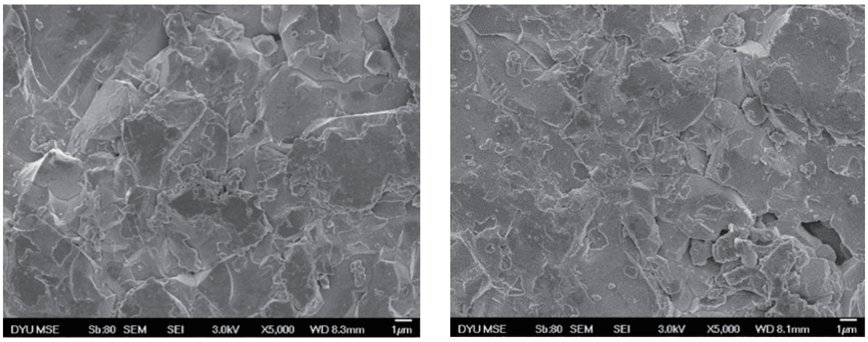
(a) (b)

Fig. 6. (Color online) TiN coating parameters on CoCrMo sample: (a) 100 ℃/500 nm and (b) 200 ℃/500 nm observed at 5000X.



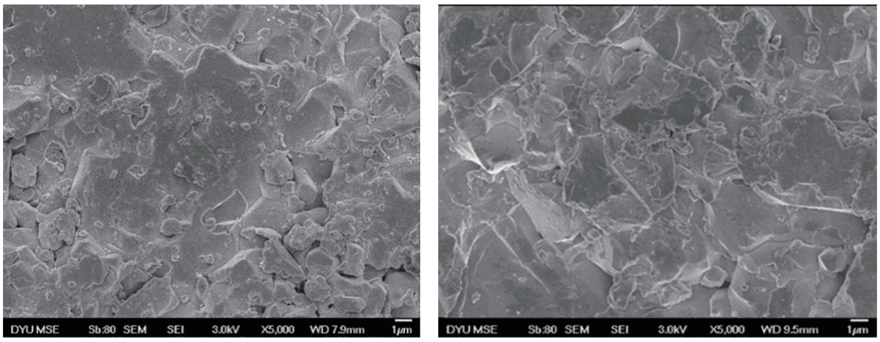
(a) (b)

Fig. 7. (Color online) TiN coating parameters on CoCrMo sample: (a) 100 ℃/750 nm and (b) 200 ℃/750 nm observed at 5000X.



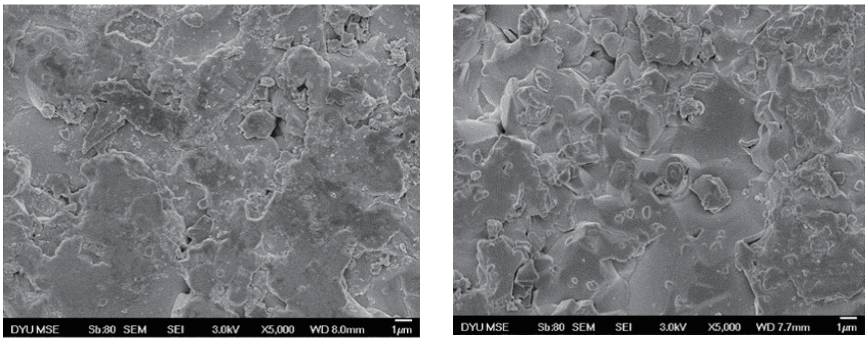
(a) (b)

Fig. 8. (Color online) TiN coating parameters on ceramic sample: (a) 100 ℃/250 nm and (b) 200 ℃/250 nm observed at 5000X.



(a) (b)

Fig. 9. (Color online) TiN coating parameters on ceramic sample: (a) 100 ℃/500 nm and (b) 200 ℃/500 nm observed at 5000X.



(a) (b)

Fig. 10. (Color online) TiN coating parameters on ceramic sample: (a) 100 ℃/750 nm and (b) 200 ℃/750 nm observed at 5000X.

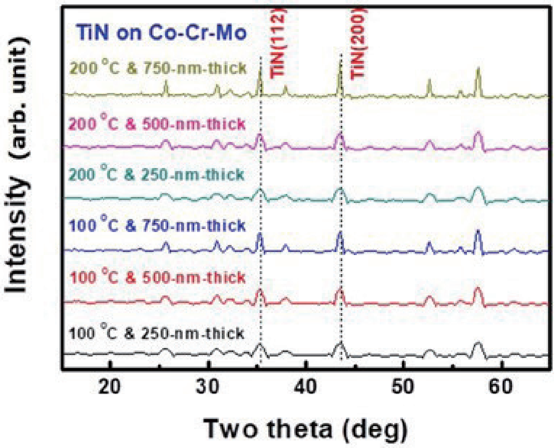


Fig. 11. (Color online) XRD patterns of TiN films on CoCrMo substrates with different substrate temperatures and film thicknesses.

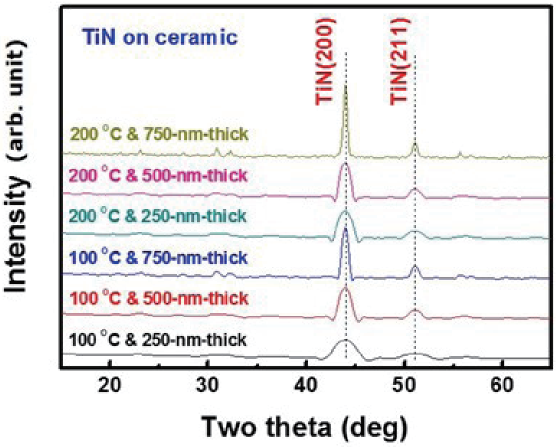


Fig. 12. (Color online) XRD patterns of TiN films on ceramic substrates with different substrate temperatures and film thicknesses.

3.3 XRD results of TiN films on CoCrMo and ceramic substrates

The XRD patterns of TiN films on CoCrMo and ceramic substrates are depicted in Figs. 11 and 12, respectively. The XRD values for TiN films are comparable for all growth settings. The XRD patterns of the TiN films deposited on CoCrMo substrates revealed two primary diffraction peaks of TiN(112) and TiN(200) planes (Fig. 11). Moreover, the two primary diffraction peaks of the TiN(200) and TiN(211) planes were present in the TiN films produced on ceramic substrates (Fig. 12). The experimental results show that the deposited TiN film will have prominent diffraction peaks on two different substrates, proving that the TiN film is indeed deposited on the substrate.

4. Conclusions

(1) From the results of hardness tests, the 250-nm-thick TiN film deposited at 100 °C had the highest hardness of 365.61 HV among the TiN-coated CoCrMo samples. In the future, we will study the sensing performance of TiN film sensors fabricated on CoCrMo alloys and the implant and sensing applications of TiN/CoCrMo materials.

(2) On the other hand, the 250-nm-thick TiN film deposited at 200 °C had the highest hardness of 376.81 HV among the TiN-coated ceramic samples. In the future, we will study the sensing performance of TiN film sensors fabricated on ceramics and the corrosion-resistant parts and sensing applications of TiN/Al_2O_3 materials.

(3) Between 250-nm-thick and 750-nm-thick TiN films on CoCrMo and ceramic substrates, the smoother surface can be achieved when the film thickness is 250 nm. According to our experimental results, the TiN film coating of 250 nm thickness exhibited the smoothest surface and the highest hardness, which will be helpful for expanding the applicability of medical implants of CoCrMo alloys. In the future, we will study the performance of sensors fabricated on TiN/CoCrMo and TiN/Al_2O_3 materials.

(4) The XRD patterns of TiN films deposited on CoCrMo alloys show two peaks of TiN(112) and TiN(200) planes. On the other hand, the films grown on ceramics have two peaks of TiN(200) and TiN(211) planes. The crystallinities in all XRD patterns of the films on the same substrates are similar to each other.

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About the Authors

Feng-Min Lai received his B.S. degree from Chinese Culture University, Taiwan, in 1991 and his M.S. and Ph.D. degrees from National Chiao Tung University, Taiwan, in 1993 and 1997, respectively. From 2002 to 2016, he was an associate professor at Da-Yeh University, Taiwan. Since 2017, he has been a professor at Da-Yeh University. His research interests are in composite materials, computer graphics, and medical aid development.
(fengmin@mail.dyu.edu.tw)

Tan-Chih Chang received his B.S. degree from Feng Chia University, Taiwan, in 1986 and his M.S. degree from the Department of Civil Engineering, Feng Chia University, Taiwan, in 1989. Since 2018, he has been an on-the-job Ph.D. student at Da-Yeh University and president of Water Conservancy Construction Co., Ltd., Taiwan. His research interests include 3D printing, the manufacture of composite materials, tensile testing in carbon fiber research, voice control, and computer graphics. (hiciv@ms43.hinet.net)