

ZrN / HYDROXYAPATITE NANOCOMPOSITE COATINGS BY CO-SPUTTERING METHOD

A. Joseph Nathanael, Jun Hee Lee, Sun Ig Hong*

Department of Nanomaterials Engineering, Chungnam National University, Daejeon, S. Korea.

*e-mail: sihong@cnu.ac.kr

Introduction

Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has been used in dentistry and medicine nowadays due to its outstanding biocompatibility and osteoconduction [1]. HA is a key inorganic component of natural bone and can speed up the bone growth [1,2]. But its mechanical strength is very poor to be used in load-bearing applications. Therefore, HA coating was deposited on the surface of metallic implants to improve the biocompatibility property [2,3]

The transition metal nitride coatings have widely used in biomedical materials in the current decade. For some requirements according to film qualities, Zr-based coatings outperform Ti based ones. Recently, Zirconium Nitride (ZrN) has been attracting interest for its excellent erosion resistance, biocompatibility, high hardness, good lubricity, and ductility properties, thereby making it potentially useful in biomedical engineering. ZrN coatings have been reported to exhibit better corrosion protection ability compared to TiN and have been used to improve the corrosion resistance of some biomaterials as stainless steels, Ti and NiTi alloys [4,5]. These properties make it an attractive biomedical coating material.

Experimental

Materials and method

Commercially pure (cp) titanium was chosen as the substrate materials. Prior to deposition, the samples were first ground with abrasive papers and then polished with diamond paste. Finally, the specimens were ultrasonically cleaned in acetone, alcohol, and distilled water successively and dried.

ZrN and HA nanocomposite coatings were deposited by RF magnetron co-sputtering method (SNTEK, RSP-5003 series) using HA and ZrN targets each of 3" diameter. The typical base pressure in the deposition chamber was about 8×10^{-6} Pa. The samples were grown in argon atmosphere at a constant working pressure (1.86 Pa) varying the substrate temperature 200 and 400 °C. The RF power applied to the target was 200W. Before the deposition, the targets were pre-sputtered for 10

min applying a RF power of 100W in Ar atmosphere.

All the samples were characterized by different methods like XRD, FESEM, AFM, nanoindentation etc., to study its different properties like structural, morphological and mechanical and biological behavior.

Results and Discussion

Structural analysis

Fig. 1 shows the XRD pattern of the nanocomposite prepared by co sputtering method. It clearly shows the reflections from HAp and ZrN phases. At 200 °C and 60 min coating the intensity of the HAp and ZrN phases were very weak. As the substrate temperature increases to 400 °C and the time increased to 120 min it is clearly observe that only ZrN and HAp peaks appear. The Ti peak is of the substrate which not dominating. Hence this condition shows a good performance in this 200W RF power.

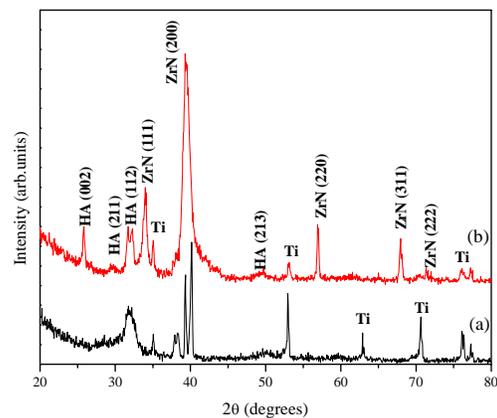


Fig.1 XRD pattern of HAp/ZrN nanocomposite coating with substrate temperature and time of (a) 200 °C & 60 min (b) 400 °C & 120

Morphological analysis

The morphological analysis (Fig 2) gives an insight in to the formation of structures due to the effect of time and temperature. The grain size is decreased for the samples prepared by higher substrate temperature.

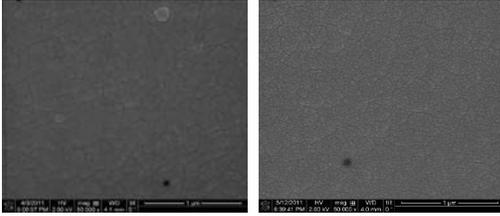


Fig.2 SEM images of HAp/ZrN nanocomposite coating with substrate temperature and time (a) 200 °C & 60 min, (b) 400 °C & 120 min.

Topographical analysis

The topographical analysis was done by AFM analysis (Fig. 3). For the low substrate temperature and short time of coating gives an overall plain surface with the presence of uneven plateaus. But for higher substrate temperature and long coating time, the films are composed of nanoparticles and the film surface is condensed and uniform structure. The well defined grain boundaries are also observed when the scanning areas are restricted to 2 μm .

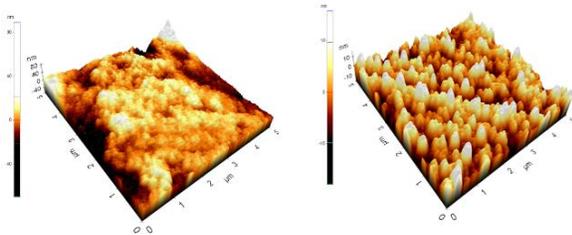


Fig.3 AFM 3D image of HAp/ZrN nanocomposite coating with substrate temperature and time of (a) 200 °C & 60 min (b) 400 °C & 120 min.

Mechanical analysis

Nanoindentation of the samples gives the overall mechanical strength of the coating. As expected the higher substrate temperature and long time coating sample shows higher hardness and modulus value. Thus this coating condition gives good mechanical strength than other conditions.

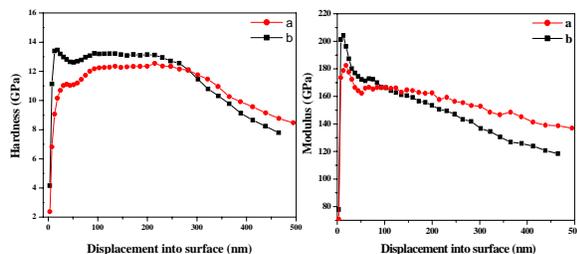


Fig.4 Hardness and Modulus of the HAp/ZrN composite coatings (a) 200 °C & 60 min, (b) 400 °C & 120 min.

Biom mineralization capacity

The higher substrate temperature induces the crystallization as observed from the XRD analysis. Also from AFM it is found that the roughness of the sample is increased for this sample which is needed for the biom mineralization ability. As expected this sample gives the good biom mineralization ability than the other samples.

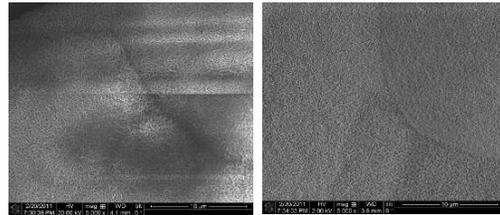


Fig.5 SBF analysis of HAp/ZrN nanocomposite coating with substrate temperature and time of (a) 200 °C & 60 min (b,c) 400 °C & 120 min

Conclusion

ZrN and HA nanocomposite coatings were deposited with different conditions on the cp Ti plates for biomedical applications. Substrate temperature and coating time has influence on the various properties of the coating. Mechanical strength and biom mineralization ability also gives impressive result for the high temperature and longer deposition time.

Acknowledgement

This work was supported by National Research Foundation (2009-0077110)

References

- Nathanael, A. J., Mangalaraj, D., Chen, P.C., Ponpandian, N. Enhanced mechanical strength of hydroxyapatite nanorods reinforced with polyethylene. *J. Nanopart. Res.*, **13** (2011) 1841–1853.
- Narayanan, R., Seshadri, S.K., Kwon, T.Y., Kim, K.H., Electrochemical nano-grained calcium phosphate coatings on Ti–6Al–4V for biomaterial applications. *Scr. Mater.*, **56** (2007) 229–232.
- Song, Y.W., Shan, D.Y., Han, E.H. Electrodeposition of hydroxyapatite coating on AZ91D magnesium alloy for biomaterial application. *Mater. Lett.* **62** (2008) 3276–3279.
- Qiu, D., Wang, A., Yin, Y. Characterization and corrosion behavior of hydroxyapatite/zirconia composite coating on NiTi fabricated by electrochemical deposition *Appl. Surf. Sci.*, **257** (2010) 1774–1778.
- Xin, Y., Liu, C., Huo, K., Tang, G., Tian, X., Chu P.K. Corrosion behavior of ZrN/Zr coated biomedical AZ91 magnesium alloy. *Surf. Coat. Technol.*, **203** (2009) 2554–2557