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Metal Release of Multilayer Coatings by Physical Vapour Deposition (PVD)

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Abstract

Orthopaedic implants are mostly fabricated by Stainless Steel, Titanium, and Ni-Cr Alloys that consist of Chromium (Cr), Cobalt (Co), Nickel (Ni) and Molybdenum (Mo). 10-15% of population are affected by metals (Ni, Co, Cr, Mo) hypersensitivity reaction. Multilayer coating by Physical Vapour Deposition (PVD) has been applied onto orthopedic implants to prevent metallic ions leaching into human body. This paper aims to study the metal ions leaching of Cr, Ni, Mo, and Co from multilayer coatings of Chromium (Cr), Chromium Nitride (CrN), Chromium Carbonitride (CrCN) and Zirconium Nitride (ZrN) by Physical Vapour Deposition (PVD). Cr, CrN, CrCN and ZrN have been successfully deposited onto stainless steel substrates by CAPVD. XRD analysis detected major peak in preferred orientation of (200) and other peaks with (111), (220), (311) for CrN cubic phase. For CrCN, XRD analysis detected only low intensity peaks of Cr7C3 and ZrN peaks with preferred orientation of (111), (200) with other peak (220), (311) and (222). A seven days metal released test by ICP-MS showed that generally all ions concentration for Ni, Co, Mo decreased from uncoated substrate to multilayer coatings except for Cr. Metal released showed higher concentration for coatings deposition with longer deposition time at 10 minutes.

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Keywords: Multilayer coating; Physical Vapour Deposition (PVD), Metal Release

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1. Introduction

Orthopaedic implants are mostly fabricated by Stainless Steel, Titanium, and Ni-Cr Alloys that consist of Chromium (Cr), Cobalt (Co), Nickel (Ni) and Molybdenum (Mo). Almost 10-15% of population are affected by metal hypersensitivity reaction, especially for Ni and followed by Co, Cr and Mo, with 22% from well-functioning implants and 60% from poorly-functioning implants. This resulting in many studies on metal ion release especially on metal-on-metal bearing hip joints made of Co–Cr–Mo alloys [1-5]. Metal ions leaching into human fluid are due to several mechanisms of corrosion such as fretting corrosion, stress corrosion and fatigue corrosion [1,2]. It has been reported concern for patients with orthopaedic implants of released metal ions level in their blood and urine [3,4].

A multilayer coating was deposited onto metal implants to prevent the leaching of metallic ions into human body. The multilayer coating will be developed to reduce the hardness from top to bottom in a gradient way to improve elastic modulus coating and extremely stable against mechanical stresses and strains and improved adhesion [6,7]. Zirconium (Zr) with excellent biocompatibility, chemical inertness and ceramic thin films of Zirconium Nitride (ZrN) with superior tribological properties with high wear resistance and low gliding friction had attracted researchers in biomedical application [8]. Chromium based coatings had been used extensively due to their excellence in corrosion resistance, hardness, as well as in bridging the differences in hardness and residual stress between softer base material and hard top coating of ZrN [9].

This paper aims to study the metal ions (Cr, Ni, Mo, Co) release of multilayer coatings of Chromium (Cr), Chromium Nitride (CrN), Chromium Carbonitride (CrCN) and Zirconium Nitride (ZrN) by Physical Vapour Deposition (PVD).

2. Experimental

2.1. Coating Deposition

The substrates were all ultrasonically cleaned in ethanol for 10 minutes to remove dirt, grease and residue from production process, followed by grounded and polished to mirror-finished. Substrates were then rinsed in deionised water and dried. Two sets of five minutes and ten minutes of deposition duration thin films were deposited by Physical Vapor Deposition (PVD) in the Argon (Ar), Nitrogen (N_2) and Methane (CH_4) gases on both sides of substrate. The geometry of multilayer coating are shown in Table 1.

Table 1. Coatings geometry.

Coating (Label)	Coating Arrangement
Chromium (Cr)	Substrate/Cr
Chromium Nitride (CrN)	Substrate/Cr/CrN
Chromium Carbonitride (CrCN)	Substrate/Cr/CrN/CrCN
Multilayer, 5 layers (ML5)	Substrate/Cr/CrN/CrCN/CrN/ZrN
Multilayer, 7 layers (ML7)	Subs./Cr/CrN/CrCN/CrN/CrCN/CrN/ZrN

2.2. Characterisation

The microstructure of the sample was analysed by Scanning Electron Microscopy (SEM). The compositions and phases present in the samples were analysed by using XRD in glancing incidence angle and Energy Dispersive X-ray (EDX). The metal release test was done by static immersion test according to JIS T 0304. Metal ions concentration was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Three test coupons from each sample (Uncoated, Chromium coated, Chromium Nitride coated, Chromium Carbonitride coated, Multilayer) were immersed in 50 ml Simulated Body Fluid (SBF) in 37°C for seven days.

3. Results and discussion

3.1. Microstructure

SEM photomicrograph as illustrated in Fig. 1 showed the cross-sectioned multilayer coating that consists of a relatively thin Chromium bond coat (a), alternate multilayer of Chromium Nitride (b), Chromium Carbonitride (c) and a top coat of Zirconium Nitride (d). SEM photomicrograph showed that the Chromium Nitride layer with dense and compact columnar microstructure while Chromium Carbonitride layer with a homogeneous microstructure that may corresponds to the presence of amorphous phases [10].

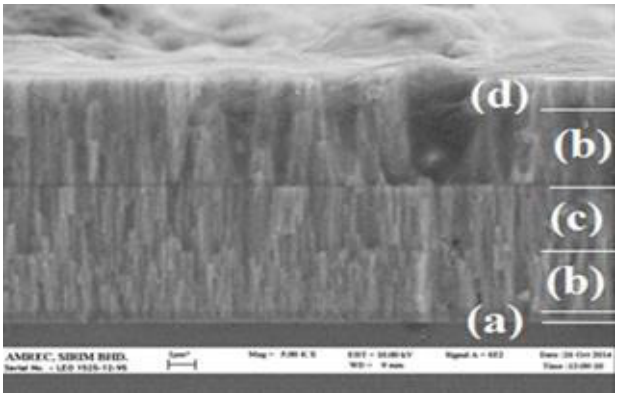

Fig. 1. SEM Photomicrograph of Multilayer Coatings

3.2. Phase detection and chemical composition

Phase detection and chemical composition were characterised by XRD and EDX. From Fig. 2, XRD analysis detected patterns of Cr, CrN, CrCN and ZrN for each monolayer. For chromium nitride layer, XRD analysis detected major peak in preferred orientation of (200) together with (111), (220), (311) planes that related to CrN cubic phase [11]. Shifted peaks to relative standard data of CrN caused by compressive stresses in the layer due to ion bombardment during deposition [12]. The Cr2N hexagonal phase also detected coexists with the CrN cubic phase. For ZrN, peaks with preferred orientation of (111), (200) were detected along with other peak (220), (311) and (222). For the multilayer coatings, some of the ZrN and CrN peaks can be observed. However, the diffraction peak of CrN (200) and ZrN (222) are not detected as compared with the single monolayer thin films due to the association of internal stress relieving that occurred in the multilayer thin films [13].

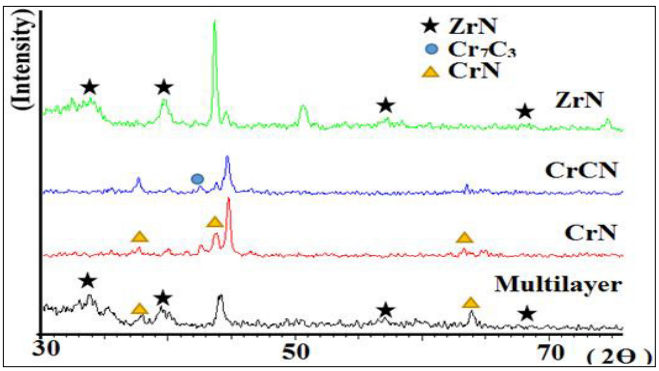

Fig. 2. XRD Diffractograms of CrN, CrCN, ZrN and Multilayer Coatings

Chemical composition by EDX method was done to further examine the phase identification together with XRD. The Cr_2N phase could be represented by coating with low chromium to nitrogen 70:30 at.% of Cr:N [14]. The summaries of EDX analysis is shown in Table 2.

Table 2. EDX Analysis

Layer	Elements	Ratio (at.%)
CrN (Cr_2N)	Cr:N_2	70:30
CrCN (Cr_7C_3)	Cr:N_2:C	37:48:15
ZrN	ZrN	48:52
Multilayer	Cr:N_2:O_2:Cr:Zr	13:14:44:28:1

3.3. Metal Release by Static Immersion Test

3.3.1. 5 Minutes Deposition Coatings

From Fig. 3, it can be seen that generally all ions concentration decreased from uncoated substrate to multilayer coatings except for Cr. Detected Cr decreased from uncoated (UC) at 0.18 µg/L to Cr coated at 0.07 µg/L then increased to 2.62 µg/L for ML7 yet below the desired maximum concentration, 6 µg/L. As opposed to Cr concentration, detected ions for Ni, Mo and Co showed better and desired results with decreased value from uncoated to ML7. The summary of ions concentration for coatings of five minutes deposition time is shown in Table 3.

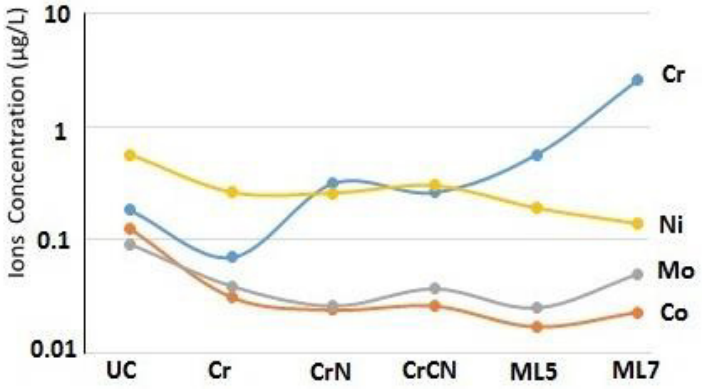

Fig. 3. Ions Concentration of Released Metal for Uncoated (UC) Substrate and Multilayer of 5 Minutes Deposition Duration

Table 3: Ions concentration of released metals for uncoated (uc) substrate and multilayers of 5 minutes deposition duration.

Substrates	Ions concentration, µg/L			
	Cr	Co	Mo	Ni
Uncoated	0.18	0.13	0.09	0.57
Cr	0.07	0.03	0.04	0.27
CrN	0.32	0.02	0.03	0.26
CrCN	0.26	0.03	0.04	0.30
ML5	0.57	0.02	0.03	0.19
ML7	2.62	0.02	0.05	0.14

3.3.2 10 minutes deposition coatings

From Fig. 4, Cr concentration showed an increased value from uncoated substrate (UC) at 0.18 µg/L to 7.52 µg/L for ML7. For Mo concentration, detected value decreased from uncoated substrate at 0.09 µg/L to 0.032 µg/L, 0.03 µg/L, 0.026 µg/L for Cr, CrN and CrCN respectively. The concentration then increased to highest value at 0.15 µg/L for ML7. However, Co and Ni concentration showed better results as desired which are decreased value from uncoated to ML7. The summary of ions concentration for coatings of ten minutes deposition time is shown in Table 4.

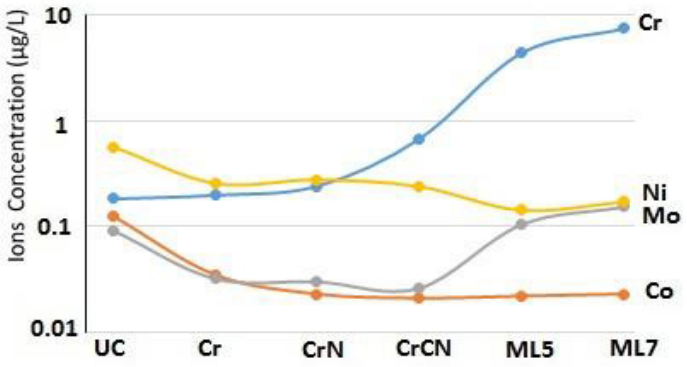

Fig. 4. Ions Concentration of Released Metal for Uncoated (UC) Substrate and Multilayer of 10 Minutes Deposition Duration.

Table 4. Ions concentration of released metals for uncoated (uc) substrate and multilayers of 10 minutes deposition duration.

Substrates	Ions concentration, µg/L			
	Cr	Co	Mo	Ni
Uncoated	0.18	0.13	0.09	0.57
Cr	0.20	0.04	0.03	0.26
CrN	0.24	0.02	0.03	0.28
CrCN	0.68	0.02	0.03	0.24
ML5	4.40	0.02	0.10	0.14
ML7	7.52	0.02	0.15	0.17

3.3.3 Effects of deposition duration

The effect of deposition duration to released ions concentrations is illustrated in Fig. 5. For all released ions, detected value showed higher concentration are at longer deposition duration which is 10 minutes compared to 5 minutes deposition. Released Cr showed similar trend for both deposition duration with increased value from substrate to multilayer coatings. Detected Mo showed a decreased value from uncoated to ML7 only at 10 minutes deposition but an increased value at 5 minutes deposition duration. Co and Ni showed a similar trend for both deposition time, detected value decreased as desired from uncoated substrate to multilayer coated.

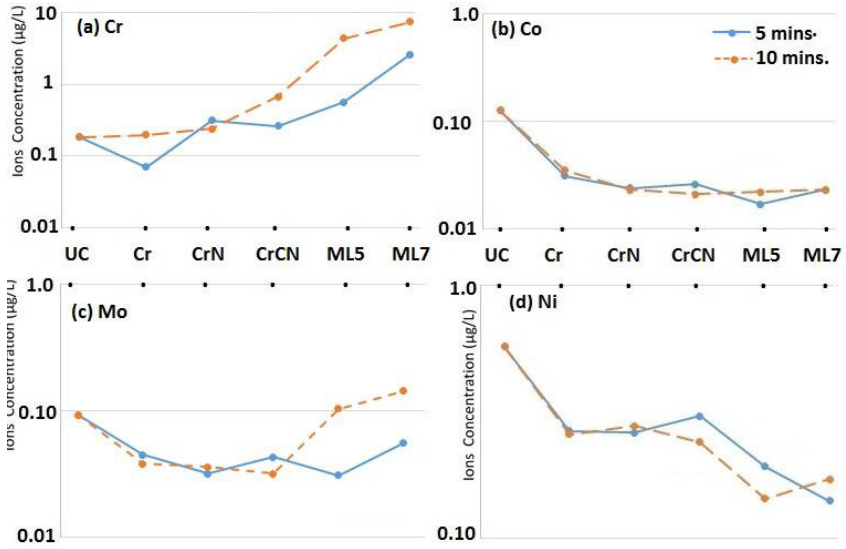

Fig. 5. Effects of Deposition Duration to Ions Concentration of Released Metal (a) Chromium, (b) Cobalt, (c) Molybdenum and (d) Nickel.for Uncoated Substrate (UC), Cr, CrN, CrCN, ML5 and ML7 Multilayers.

4. Conclusion

Chromium (Cr), Chromium Nitride (CrN), Chromium Carbonitride (CrCN) and Zirconium Nitride (ZrN) have been succesfully deposited onto stainless steel substrates. XRD analysis detected major peak in preferred orientation of (200) and other peaks with (111), (220), (311) planes that related to CrN cubic phase along with hexagonal Cr_2N phase. For CrCN, XRD analysis detected only low intensity peaks of Cr_7C_3. For ZrN, peaks with preferred orientation of (111) and (200) with other peak (220), (311) and (222) were detected. A seven days metal released test by ICP-MS showed that generally all ions concentration for Ni, Co, Mo decreased from uncoated substrate to multilayer coatings except for Cr. Metal released showed higher concentration for coatings deposition with longer deposition time at 10 minutes.

References

[1] Yoshimitsu Okazaki, Emiko Gotoh: Metal release from stainless steel, Co–Cr–Mo–Ni–Fe and Ni–Ti alloys in vascular implants: Corrosion Science 50 (2008) 3429–3438.
[2] J.J. Jacobs, C. Silverton, N.J. Hallab, A.K. Skipor, L. Patterson, J. Black, J.O. Galante, Metal release and excretion from cementless titanium alloy total knee replacements, Clin. Orthop. Relat. Res. 358 (1999) 173–180.
[3] I.B. McPhee, C.E. Swanson, Metal ion levels in patients with stainless steel spinal instrumentation, Spine 32 (2007) 1963–1968.
[4] N. Hallab, K. Merritt, J.J. Jacobs, Metal sensitivity in patients with orthopaedic implants, J. Bone Joint Surg. Am. 83A (2001) 428–436.
[5] J.J. Jacobs, A.K. Skipor, L.M. Patterson, N.J. Hallab, W.G. Paprosky, J. Black, J.O. Galante, Metal release in patients who have had a primary total hip arthroplasty. A prospective, controlled, longitudinal study, J. Bone Joint Surg. Am. 80A (1998) 1447–1458.
[6] Reich J. Hovy L, Lindenmaier HL, Zeller R, Schweisau J, Thomas P, Grupp TM. PraklinischeErgebnissebeschichteterKnieiimplantate fur Allergiker. Orthopade.2010 Mai; 39(5): 495-502
[7] Santane AE, Relating hardness-curve shapes with deformation mechanisms in TiAlN thin films indentation. Materials Science and Engineering A 406(2005) 11-18
[8] Yunchang Xin, Chenglong Liu, Kaifu Huo, Guoyi Tang, Xiubo Tian, Paul K. Chu, Corrosion behavior of ZrN/Zr coated biomedical AZ91 magnesium alloy, Surface & Coatings Technology 203 (2009) 2554 - 2557.
[9] B. Warcholin´ski, A. Gilewicz, Z. Kuklin´ski, P. Myslin, Arc-evaporated CrN, CrN and CrCN coatings, Vacuum 83 (2009) 715 - 718.
[10] G.G. Fuentes, M.J. Díaz de Cerio, J.A. García, R. Martínez, R. Bueno, R.J. Rodríguez, M. Rico, F. Montalá, Yi Qin : Gradient CrCN cathodic arc PVD coatings: Surface & Coatings Technology 203 (2008) 670–674
[11] J. Romero, E. Martinez, J. Esteve, A. Lousa: Nanometric chromium nitride-chromium carbide multilayers by r.f. magnetron sputtering: Surface and Coatings Technology 180 – 181 (2004) 335–340

[12] B. Warcholinski , A. Gilewicz, Z. Kuklin ski, P. Myslinski. Arc-evaporated CrN, CrN and CrCN coatings, Vacuum 83 (2009) 715–718
[13] Sung-Hsiu Huang, Siao-Fan Chen, Yu-Chu Kuo, Chaur-Jeng Wang, Jyh-Wei Lee, Yu-Chen Chan, Hsien-Wei Chen, Jenq-Gong Duh, Tsung-Eong Hsieh : Mechanical and tribological properties evaluation of cathodic arc deposited CrN/ZrN multilayer coatings: Surface & Coatings Technology 206 (2011) 1744–1752
[14] B. Warcholinski n , A. Gilewicz, J. Ratajski: Cr2N/CrN multilayer coatings for wood machining tools: Tribology International 44 (2011) 1076–1082