Surface & Coatings Technology 204 (2010) 2193–2196

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Influence of interlayers on corrosion resistance of diamond-like carbon coating on magnesium alloy

Guosong Wu [a,b,*], Lili Sun [a], Wei Dai [a], Lixin Song [b], Aiying Wang [a,*]

[a] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China
[b] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

ARTICLE INFO

Article history:
Received 2 March 2009
Accepted in revised form 5 December 2009
Available online 29 December 2009

Keywords:
Magnesium alloy
DLC
Interlayer
Sputtering
Corrosion

ABSTRACT

Diamond-like carbon coating (DLC) was deposited on AZ31 magnesium alloy by ion beam deposition technique in this study. A columnar Cr layer with a (110) preferred texture and a columnar CrN layer with a (111) preferred texture were applied as interlayers in the DLC coating/AZ31 substrate systems. The addition of these interlayers improved the adhesion between coating and substrate effectively, but did not enhance the corrosion resistance of the DLC/AZ31 systems due to the formation of galvanic cell between substrate and interlayer in the region of through-thickness defects in 3.5 wt.% NaCl solution. In addition, the effect of bias voltage on the corrosion resistance of CrN/Cr coatings on magnesium alloys was investigated. Although the application of bias voltage induced the coating denser, it was still difficult for CrN/Cr coating to reduce the corrosion current density of AZ31 due to the large difference between coating and substrate in galvanic series.

1. Introduction

There is a growing interest in magnesium alloys as structural materials for the aerospace, automotive and electronic industries due to their light weight. However, the poor corrosion resistance and wear resistance of magnesium alloys limit their further application [1]. Diamond-like carbon (DLC), which owns a high mechanical hardness and a chemical inertness, has been applied as protective coatings in areas such as optical windows, magnetic storage disks, car parts, biomedical coatings and as micro-electromechanical devices [2]. In recent years, some researchers have attempted to use DLC as a protective coating for magnesium alloys to improve their mechanical and anti-corrosion properties [3–7].

Yamauchi et al. deposited DLC coatings on Mg–Li alloys using Si layer as a buffer to relieve the influence of the physical properties difference between coating and substrate. Unfortunately, both the adhesion between coating and substrate and the corrosion resistance of the coated sample in the artificial perspiration were not improved. At the end of their paper, they considered that it is possible that a different element (e.g. Cr) would act as a more effective interlayer [3]. Therefore, we selected Cr and CrN as interlayers in the DLC/magnesium alloy system in this study according to their proposal. Subsequently, the effect of interlayers on the corrosion resistance of DLC on magnesium alloy was investigated.

2. Experimental

As-extruded AZ31 plates were first ground with emery paper up to 1500# and then polished with Al_2O_3 paste (average size 1 μm). A hybrid ion beam deposition system, including a linear ion source and a magnetron sputtering source, was performed to prepare DLC coatings on AZ31 substrates. Substrates were ultrasonically washed in pure alcohol for 5 min before they were sent into the vacuum chamber. When the base pressure of the chamber was below 2×10^{-5} Torr, the ion source with Ar gas was applied to etch the substrate for 30 min. Next, the magnetron sputtering source was used to prepare the interlayers with Ar as sputtering gas and N_2 as reactive gas and the linear ion source was used to prepare the diamond-like carbon coating with CH_4 as source gas. Bias voltage was applied at pulse mode with frequency of 350 kHz. The substrate rotated at a speed of 4.2 rpm in the coating deposition. The specific parameters of the coating deposition are shown in Table 1. The chamber temperature at the stage of Cr sputtering and CrN sputtering was about 50 °C and that at the stage of DLC deposition was about 100 °C. Besides, the chamber pressures at the stage of Cr sputtering, CrN sputtering and DLC deposition were about 1.4×10^{-3} Torr, 3.2×10^{-3} Torr and 1.4×10^{-3} Torr, respectively. In this paper, the elastic modulus and hardness of DLC film prepared under the above condition are 144.8 GPa and 17.4 GPa, respectively.

Field emission scanning electron microscope (FESEM) was performed to characterize the cross section and surface morphology of the obtained coatings. Energy dispersive X-ray spectrometer (EDS) was used to test the element distribution of coatings. X-ray diffraction meter with Cu Kα radiation was used to study the crystal structure of the obtained coatings. The adhesion properties of the coating/

* Corresponding authors. Tel./fax: +86 57486685171.
E-mail addresses: wugsjd@126.com (G. Wu), aywang@nimte.ac.cn (A. Wang).

0257-8972/$ – see front matter
doi:10.1016/j.surfcoat.2009.12.009

Table 1
Experimental parameters in the preparation process.

Sample	Layer	Current (A)		Gas flux (sccm)			Deposition time (min)	Bias voltage (V)
		Sputtering source	Ion source	Ar	N_2	CH_4		
1	Cr	3		40			30	
	CrN	3		40	40		60	
2	Cr	3		40			30	−300
	CrN	3		40	40		60	−300
3	DLC		0.2			40	60	−100
4	Cr	3		40			30	
	DLC		0.2			40	60	−100
5	CrN	3		40	40		30	
	DLC		0.2			40	60	−100
6	Cr	3		40			15	
	CrN	3		40	40		15	
	DLC		0.2			40	60	−100

substrate systems were investigated by a scratch tester. The normal load of the indenter was linearly ramped from the minimum to the maximum during scratching. Here, the minimum load and the maximum load were 0.1 N and 20 N, respectively. In the test, the scratch length was 5.00 mm and the scratch speed was 0.2 mm/s. For the electrochemical investigation, the experiments were controlled by an AUTOLAB PGSTAT302 advanced electrochemical system, using the conventional three-electrode technique. The potential was referred to a saturated calomel electrode (SCE) and the counter electrode was a platinum sheet. Each sample was masked by paraffin waxes with the surface area of 0.5×0.5 cm^2 exposed in 3.5 wt.% NaCl solution. The potential was scanned from −1.65 V (in the cathodic region) to where the anodic current increased dramatically (in the anodic region). These tests were carried out at 1 mV/s at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of all samples prepared in this study. In the curve of DLC/AZ31, there are no peaks of carbon occurred, which means that this coating exists as an amorphous state. According to the XRD patterns of AZ31 and DLC/AZ31, it is determined that the Cr layer presented the (110) preferred texture and the CrN layer presented the (111) preferred texture in the systems of DLC/Cr/AZ31, DLC/CrN/AZ31 and DLC/CrN/Cr/AZ31. As shown in the curves of CrN/Cr/AZ31(none) and CrN/Cr/AZ31(−300 V), the intensity of peak CrN(111) and peak Cr(110) was decreased and the intensity of peak CrN(200) was increased when the bias voltage was applied in the deposition process.

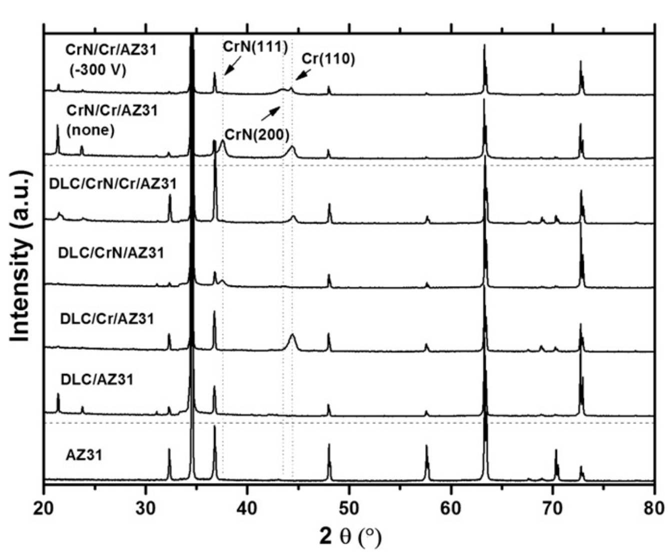

Fig. 1. XRD patterns of all samples prepared in this study.

Fig. 2(a) and (b) shows the cross sections of two CrN/Cr coatings on Si substrate, which were prepared under different bias voltages. In each image, two layers, CrN(top) and Cr(bottom), can be distinguished clearly and each layer exhibited a developed columnar structure. Fig. 2(c) and (d) shows the surface morphologies of two above coatings on AZ31 substrate. With the application of bias voltage, the surface of the CrN/Cr coating turned dense with the decrease of cracks and pores. The insets of these two images show the surface morphology at a high magnification. It can be observed that the columnar microstructure of the CrN/Cr film was more compact in the case of applied substrate bias. Fig. 2(e), (f), (g) and (h) shows the cross sections of DLC, DLC/Cr, DLC/CrN and DLC/CrN/Cr on Si substrate, respectively. The insets in Fig. 2(e) and (h) give the element distribution along the designated line from substrate to coating, which also proves the formation of the carbon films on substrates. These amorphous DLC layers are smooth and dense compared with the columnar structure of the interlayers. However, some big particles, one of which is shown in Fig. 2(e), can be found on the surface.

Fig. 3 shows the critical loads of the coated samples in the scratch test in this study. With the addition of Cr and CrN interlayers, the critical load of the DLC/AZ31 system became larger. Especially for the DLC/Cr/AZ31 system, it owned the highest critical load among all samples. The scratch test is a traditional method to assess the adhesion strength of coating/substrate systems. A loaded diamond stylus is drawn across the coated surface at continuously increasing loads until the coating is stripped from the substrate at a critical load. The adhesion can be thus evaluated by this critical load. The higher the critical load is, the better the adhesion is. Therefore, the result of the scratch test indicates that the addition of Cr film and CrN film as buffers is helpful to the improvement of the adhesion between coating and substrate.

Fig. 4 gives the polarization curves of all samples in 3.5 wt.% NaCl solution. Generally, the cathodic polarization curve is assumed to represent the cathodic hydrogen evolution through water reduction, while the anodic curve represents the dissolution of the tested material. The corrosion current density and corrosion potential, which are critical parameters to evaluate the anti-corrosion property of materials, were derived directly from the region in the polarization curves by Tafel region extrapolation. The corrosion potentials and corrosion current density are shown in Table 2. Based on these electrochemical parameters, it is concluded that these coatings have changed the corrosion behavior of AZ31 substrate in NaCl solution. The CrN/Cr coatings didn't reduce the corrosion current density of AZ31. In contrast, those prepared without bias voltage increased the corrosion current density of AZ31 from 7.323×10^{-5} A/cm^2 to 1.022×10^{-3} A/cm^2. The single DLC coating lowered the corrosion current density of AZ31 from 7.323×10^{-5} A/cm^2 to 1.715×10^{-5} A/cm^2. However, the addition of interlayers made the corrosion current density of DLC/AZ31 higher, that is to say, these interlayers decreased the corrosion resistance of DLC/AZ31.

Altun and Sen proposed that some through-thickness defects in the coating are the main factor to influence the corrosion resistance of the PVD coating/magnesium substrate system in his study [8,9]. In our study, some small cracks and pores are also existed in the prepared coating (e.g. those shown in Fig. 2(c) and (d)). Both Cr and CrN have higher corrosion potentials than AZ31 in 3.5 wt.% NaCl solution [10,11], so local galvanic corrosion easily occurs at the interface of coating and substrate in the defects. Although bias voltage induced more ions to impact the surface and accordingly reduced more defects, the CrN/Cr coating prepared using bias voltage didn't reduce the corrosion current density of AZ31 due to the large corrosion driving force provided by the large difference between coating and substrate in galvanic series. According to the fact that the corrosion

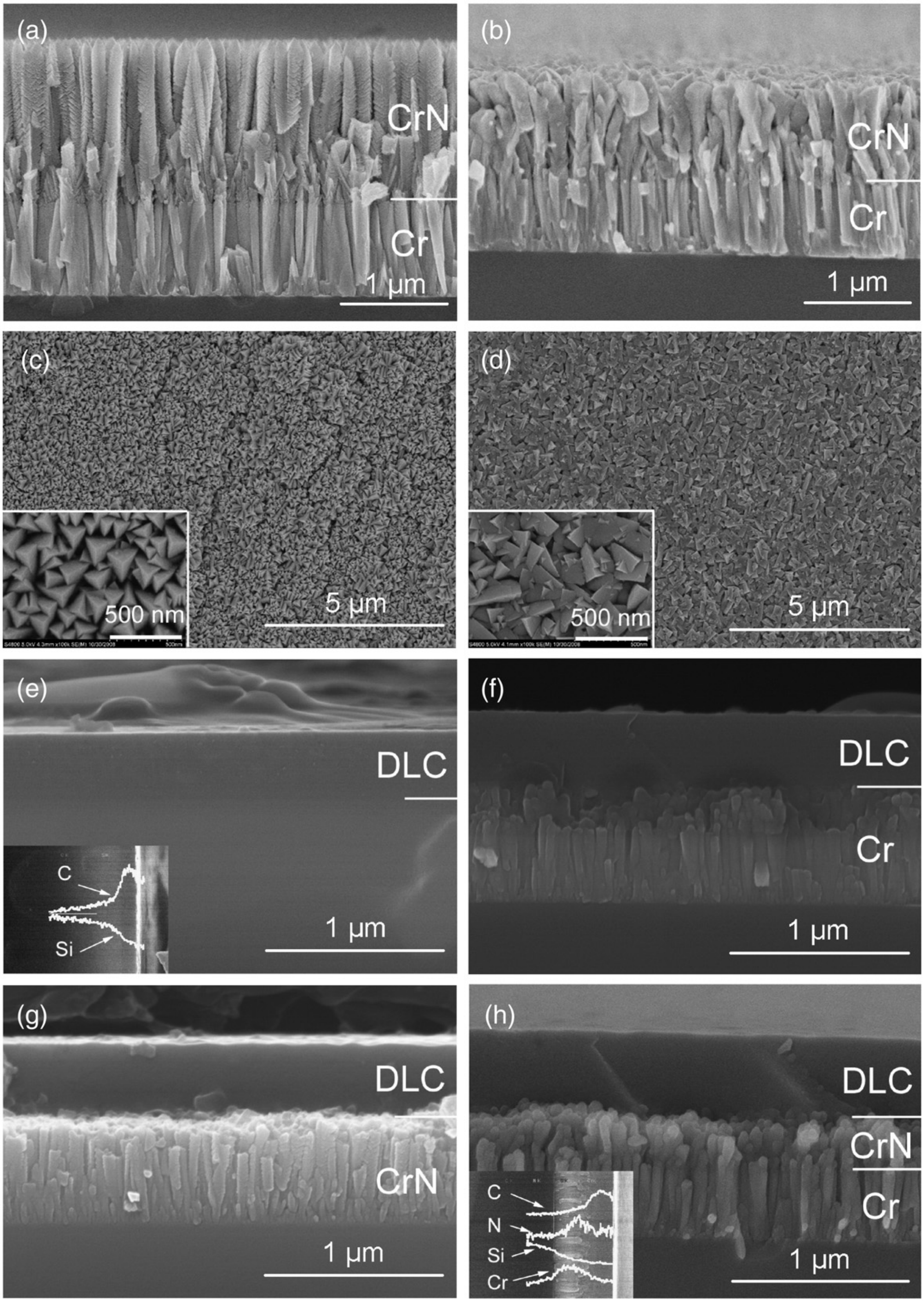

Fig. 2. Cross section and surface morphologies of all coatings prepared in this study: (a) and (c) CrN/Cr, no bias voltage applied, (b) and (d) CrN/Cr, bias voltage of −300 V, (e) DLC, (f) DLC/Cr, (g) DLC/CrN, and (h) DLC/CrN/Cr.

potential of DLC/AZ31 is close to that of AZ31, it can be further concluded that there must be several through-thickness defects in the DLC coating. Thus, for DLC/Cr/AZ31, DLC/CrN/AZ31 and DLC/CrN/Cr/AZ31, paths are formed for corrosive media to arrive the interface of coating and substrate if some defects in each layer connect together. The insulative DLC is not easy to form galvanic cell with AZ31, but when the interlayers, conductive Cr and CrN, are added, galvanic cell will be formed between interlayers and substrate. Therefore, the corrosion resistance of the whole coating/substrate system is decreased.

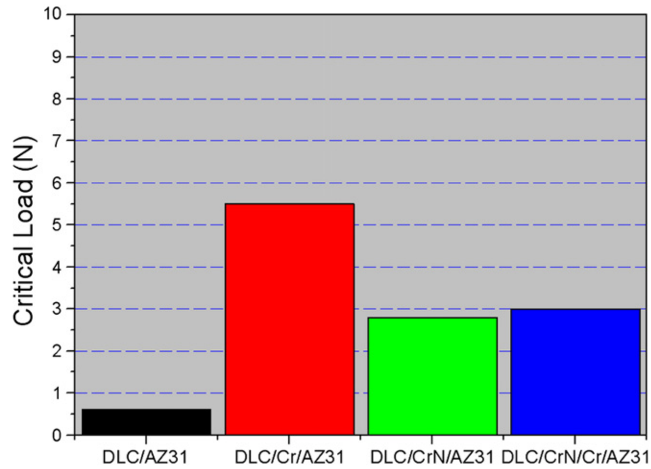

Fig. 3. Critical loads of the coated samples in the scratch test.

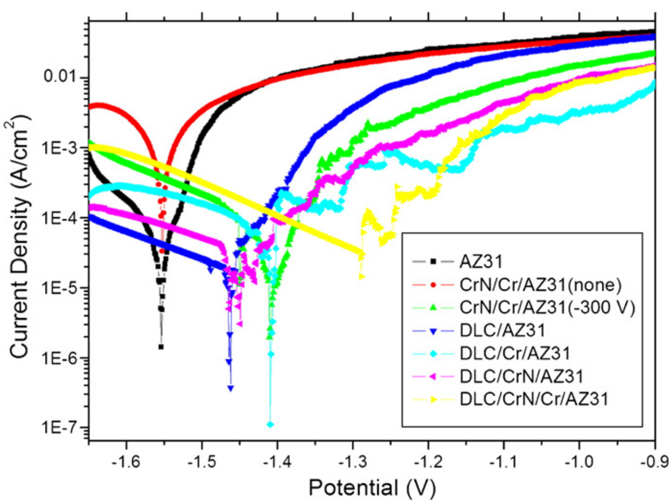

Fig. 4. Polarization curves of all samples prepared in this study.

Table 2
Electrochemical parameters obtained from the polarization curves.

Sample	Corrosion potential (V)	Corrosion current density (A/cm^2)
AZ31	−1.556	7.323×10^{-5}
CrN/Cr/AZ31(none)	−1.551	1.022×10^{-3}
CrN/Cr/AZ31(−300 V)	−1.406	8.301×10^{-5}
DLC/AZ31	−1.462	1.715×10^{-5}
DLC/Cr/AZ31	−1.407	6.809×10^{-5}
DLC/CrN/AZ31	−1.449	3.249×10^{-5}
DLC/CrN/Cr/AZ31	−1.289	3.262×10^{-5}

4. Conclusions

In summary, DLC, DLC/Cr, DLC/CrN and DLC/CrN/Cr have been deposited on AZ31 magnesium alloy by a hybrid ion beam deposition system that includes a linear ion source and a magnetron sputtering source. The addition of Cr and CrN as interlayers improved the adhesion between coating and substrate effectively, but did not enhance the corrosion resistance of the DLC/magnesium alloy systems in 3.5 wt.% NaCl solution due to the formation of galvanic cell between substrate and interlayer in the region of through-thickness defects.

Acknowledgements

This study was supported by China Postdoctoral Science Foundation (Grant No. 20080430694), Ningbo Municipal Nature Science Foundation (Grant No. 2007A610028) and Shanghai Postdoctoral Scientific Program (Grant No. 08R214156).

References

[1] J.E. Gray, B. Luan, J. Alloys Compd. 336 (2002) 88.
[2] J. Robertson, Mat. Sci. Eng. R 37 (2002) 129.
[3] N. Yamauchi, N. Ueda, A. Okamoto, Surf. Coat. Technol. 201 (2007) 4913.
[4] N. Yamauchi, K. Demizu, N. Ueda, Thin Solid Films 506–507 (2006) 378.
[5] N. Yamauchi, K. Demizu, N. Ueda, Surf. Coat. Technol. 193 (2005) 277.
[6] J. Choi, J. Kim, S. Nakao, Nucl. Instrum. Methods B 257 (2007) 718.
[7] J. Choi, S. Nakao, J. Kim, Diam. Relat. Mater. 16 (2007) 1361.
[8] H. Altun, S. Sen, Surf. Coat. Technol. 197 (2005) 193.
[9] H. Altun, S. Sen, Mater. Design 27 (2006) 1174.
[10] G. Wu, A. Wang, K. Ding, Trans, Nonferrous Met. Soc. China 18 (2008) s329.
[11] Z. Zhang, O. Rapaud, N. Bonasso, Vacuum 82 (2008) 1332.