Effect of ALD passivation layer on the corrosion and mechanical properties of PVD-based hard coatings

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1.   Introduction

Hard coatings have been extensively applied in various industrial applications such as cutting, forming and casting tools in order to increase the life time of such components and enhance the tools performance due to their high hardness, good chemical and thermal stability, and significant wear resistance [1-5]. So far, hard coatings have been synthesized by a number of techniques, such as plasma-assisted chemical vapor deposition (PECVD), magnetron sputtering (MS), arc ion plating (AIP), pulsed laser deposition (PLD), ion beam assisted deposition (IBAD), and their advanced deposition techniques including high power impulse magnetron sputtering (HIPIMS) [6-7]. Hard coatings present intrinsic defects (columnar structures, pinholes, pores, discontinuities) which can affect the corrosion behavior, especially when substrates are active alloys like steel or in a wear-corrosion process. Atomic layer deposition (ALD), a CVD derived method with a broad spectrum of applications, has shown great potential for corrosion protection of high-precision metallic parts or systems [8-10]. In ALD deposition, the precursors are introduced with alternated and separated pulsing to a substrate surface. The precursor pulses are isolated by inert gas purging so that they can only interact on the surface. The growth proceeds through cyclic repetition of self-limiting surface reactions, which leads to the thin films possess high quality, low defect density, uniformity, low-temperature processing and exquisite thickness control. These merits make ALD an ideal candidate for the fabrication of excellent oxide passivation layer which can block the pinhole and other defects left in the coating structure to improve the corrosion protection of hard coatings.

In this study, ALD passivation layers such as Al_2O_3, TiO_2, and their nanolaminated films were inserted in CrN-based hard coatings to improve the mechanical properties as well as corrosion properties of CrN-based hard coatings. The kinds of ALD interfacial layer and its periodicity significantly affects the mechanical and corrosion properties of CrN-based hard coatings. The influence of the ALD interlayer addition on the microstructure, surface roughness, mechanical properties and corrosion behaviors were systemically investigated

2.   Experimental procedure

Firstly, Cr adhesion layer was deposited on the ultrasonic cleaned single crystalline Si wafers and SUS304 substrate to improve the coating adhesion. The CrN layer was deposited from a Cr target (99.99%) in Ar and N_2 gas by utilizing a coating system with a modulated pulse power (HIPIMS+ power, Hauzer Techno Coating BV). The CrN layer thickness was controlled by adjusting the deposition time. Secondly, a dense Al_2O_3 layer were deposited on the top of CrN layer by using trimethylaluminium (TMA) and H2O precursors at the temperature of 200°C in ALD system. During the deposition, 50 sccm Ar gas was continuously supplied into the reactor. For a uniform precursor supply, the canisters containing TMA and H_2O were maintained at a temperature of 25 °C and 10 °C, respectively. The growth sequence was consisted of a 0.5 s TMA pulse, 10 s N_2 purge, 1 s H_2O pulse and 10 s N_2 purge. The Al_2O_3 layer thickness was controlled by adjusting deposition cycles. Thirdly, a top layer of CrN was deposited on the Al_2O_3 layer using the same deposition conditions. For comparison, the pure CrN coating and CrN/Al_2O_3/CrN multilayered coatings with Al_2O_3 layer thickness of 5 nm and 10 nm and different positions in the coatings were deposited by adjusting the HIPIMS deposition time and ALD deposition cycles.

X-ray diffractometer (XRD, D8-Discovery Brucker, 40kV) with 1.54 Å Cu-Kα radiations was employed to examine the crystal structure of the coatings. The surface and cross section micrographs of the coatings were studied by using scanning electron microscope (SEM, Hitachi, S-4800, 15 KV). The mechanical properties of the coatings were investigated using a nano-indentation tester (Hysitron, TI 950 TriboIndentor) and microhardness tester with a Knoop indenter (Mastsuzawa, MMT-7). The residual stress of the coatings was obtained from a laser-based curvature measurement of the coated Si-substrates by calculating using the Stoney's equation [30]. The electrochemical corrosion behavior of the coatings was investigated by a potentiodynamic polarization test. The potentiodynamic polarization curves of the samples were obtained utilizing a potentiostat in 3.5 wt.% solution of NaCl at room temperature. A silver/silver chloride and platinum (Pt) mesh were used as a reference electrode and a counter electrode, respectively.

3.   Results and discussion

Pure CrN coating, the CrN coating with 5 nm Al_2O_3 layer inserted near the substrate, the CrN coating with 10 nm Al_2O_3 layer inserted near the substrate, and the CrN coating with 10 nm Al_2O_3 layer inserted near the coating surface were denoted by sample 1 (CrN), sample 2 (CrN-Al_2O_3, 5 nm down), sample 3 (CrN-Al_2O_3, 10 nm down) and sample 4 (CrN- Al_2O_3, 10 nm up), respectively.

The potentiodynamic polarization tests were conducted to investigate the corrosion behavior of different samples. **Fig. 1** shows the polarization curves of the bare stainless steel substrate, pure CrN coated and CrN/Al_2O_3/CrN coated stainless steel, respectively.

Fig. 1 (a) shows the corrosion potentials (E_{Corr}), and corrosion current density (I_{Corr}) which was calculated using Tafel equation, respectively. The E_{Corr} increased and the I_{Corr} decreased by applying CrN coating, respectively, which means the CrN coating protected the substrate from corrosive media. With 5 nm Al_2O_3 interlayer addition by ALD, the E_{Corr} continuously increased while the I_{Corr} continuously decreased, respectively, as compared to that of the CrN coating. The thickness increase of the Al_2O_3 layer (sample 3) and implantation position change to near the coating surface (sample 4) resulted in further increase of the E_{Corr} and decreased of the I_{Corr}, respectively, which indicated the significant improvement for corrosion resistance of the CrN coatings.

Fig. 2 shows the schematic illustrations of the corrosion behavior of the pure CrN coated and CrN/Al_2O_3/CrN coated stainless steel substrates, respectively. The improvement effects of Al_2O_3 interlayer on corrosion behavior of CrN coatings may attribute to two dominant reasons: (1) The dense Al_2O_3 interlayer acted as a perfect insulating barrier for blocking the electron transportation in the coatings and the current flow from anode to cathode, which decreased the corrosion current density and declined the electron exchange rate and dissolution rate of anode metal ions at the corrosion interface. (2) The consecutive Al_2O_3 interlayer with low defects acted as an excellent barrier for blocking the diffusion of corrosive substance, such as chlorine ions. The chlorine ion plays an important role in corrosion process because of its destruction capability to the passive film which was spontaneously formed to increase the resistance against corrosion. Due to the small ion radius, the chlorine ions can easily diffuse through the columnar grain boundaries, intrinsic pinholes and defects in the coatings, and react with the metal ions as soluble compounds.
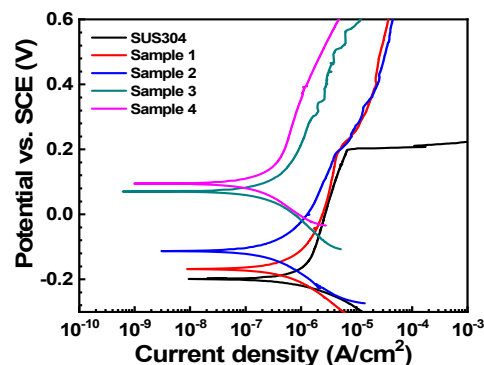

Fig. 1. Potentiodynamic polarisation curves of the bare stainless steel substrate, pure CrN coated and CrN/Al2O3/CrN coated stainless steel, respectively.
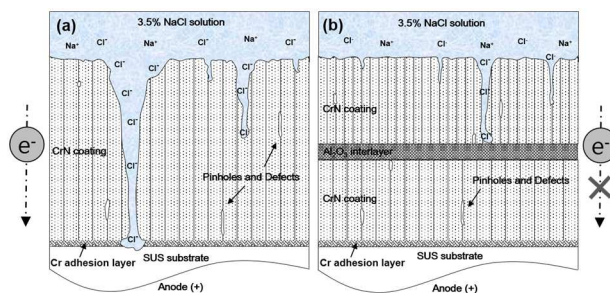

Fig. 2. Schematic illustrations of corrosion behavior of (a) the pure CrN coating and (b) CrN/Al_2O_3/CrN multilayered coating in 3.5 wt.% NaCl solution, respectively.

4.   Conclusion

Pure CrN and CrN/Al_2O_3/CrN multilayereded coatings were synthesized by a hybrid deposition process of high power impulse magnetron sputtering (HIPIMS) and atomic layer deposition (ALD). The following conclusions were obtained:

1) The corrosion resistance of the CrN coatings were greatly improved by low-defects Al_2O_3 interlayer addition, which were attributed to the Al_2O_3 interlayer acted as a perfect insulating barrier for blocking the electron transportation in the coatings and an excellent barrier for blocking the diffusion of corrosive substance, such as chlorine ions.

2) The thickness increase of the Al_2O_3 interlayer and the intercalation position change to near the coating surface resulted in further improvements of the mechanical properties and corrosion resistance.

Reference

1)   P. H. Mayrhofer, C. Mitterer, L. Hultman and H. Clemens, Prog. Mater. Sci. 51 (2006) 1032-1114.
2)   S. Veprek, J. Nanosci. Nanotechnol. 11 (2011) 14-35.
3)   J. Musil, Surf. Coat. Tech. 207 (2012) 50-65.
4)   S. –K. Tien, J. –G. Duh and J. –W. Lee, Surf. Coat. Tech. 201 (2007) 5138–5142.
5)   Y. K. Jeong, M. C. Kang, S. H. Kwon, K. H. Kim, H. G. Kim and J. S. Kim, Curr. Appl Phys. 9 (2009) S141-S144.
6)   J. Lin, B. Wang, Y. Ou, William D. Sproul, Isaac Dahan and John J. Moore, Surf. Coat. Tech. 216 (2013) 251-258.
7)   T. F. Zhang, Q. M. Wang, J. Lee, P. Ke, R. Nowak and K. H. Kim, Surf. Coat. Tech. 212 (2012) 199-206.
8)   C. X. Shan, X. Hou and K. L. Choy, Surf. Coat. Technol. 202 (2008) 2399-2402.
9)   E. Marin, L. Guzman, A. Lanzutti, L. Fedrizzi and M. Saikkonen, Electrochem. Commun. 11 (2009) 2060-2063.
10)   C. X. Shan, X. Hou, K. –L. Choy and P. Choquet, Surf. Coat. Technol. 202 (2008) 2147-2151.