Corrosion resistance of CrAlN and TiAlN coatings deposited by lateral rotating cathode arc

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Abstract

In this work, CrAlN and TiAlN coatings were deposited on stainless steel substrates by a vacuum arc reactive deposition process from two lateral rotating elemental aluminum and chromium or titanium cathodes in a flowing pure nitrogen atmosphere. The composition and crystalline structure of the as-deposited coatings was analyzed by energy dispersive analysis of X-rays (EDX) and X-ray diffraction (XRD), respectively. The corrosion resistance of the CrAlN-coated and TiAlN-coated samples in a 3 wt.% NaCl solution was evaluated and compared by electrochemical potentiodynamic polarization method. It was found that both the CrAlN and TiAlN coatings exhibited their best corrosion resistance, respectively, at a composition with Cr/Al or Ti/Al atomic ratio of around 1:1, while the CrAlN coatings showed an evidently better corrosion resistance than the TiAlN coatings.

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1. Introduction

Since the commercialization of physical vapor deposited (PVD) TiN coatings in early 1980s, hard coatings based on transition metal nitrides have been successfully used for materials protection and particularly to improve cutting tools lifetime. Traditionally, hard coatings have mainly been applied to cutting tools to give good protection against abrasive wear, and thus lengthen tool life. Nowadays, new coatings have to be more and more multifunctional in order to meet industrial needs. In many applications, the coated parts are frequently exposed to an aggressive working environment, for instance, a Cl− containing corrosive medium, particularly in a maritime region, due to the strong effects of Cl− in promoting localized corrosion. In these cases it is additionally desirable that the coating should provide the substrate with an improved corrosion resistance [1,2].

Currently, a wide range of PVD hard coatings is available for a variety of applications. TiN is the first generation of PVD hard coating and is still being widely used. As one of the major milestones in the advances of hard coating development, TiAlN has been commercially very successful due to its significantly improved oxidation resistance and hardness over TiN [3–5]. To date, titanium-based coatings have defined the benchmark of hard coatings. However, it is well known that in an oxidation or corrosive environment Ti element often forms a porous non-protective oxide scale [6], and therefore the oxidation and corrosion resistance of titanium-based coatings is limited. Recently, the new formula of Ti-free PVD coatings has already been explored by various research groups worldwide [7,8]. CrN-based multicomponent nitride is a typical example. Similar to TiN, chromium nitride (CrN) has been successfully applied to the molding dies, wear components, and cutting tools. CrN is known to be superior to TiN in corrosion and wear resistances, friction behavior, and toughness [9–12]. In comparison with TiN-based coatings (e.g. TiAIN), better tribological properties and toughness of CrN-based multicomponent coatings (e.g. CrAIN) could be expected. Recently, CrAIN coatings have been reported exhibiting even higher oxidation resistance than TiAIN [13,14], as both the chromium and aluminum could form protective oxides which suppressed oxygen diffusion. Similarly, a better corrosion resistance of CrAIN coatings could also be expected than that of TiAIN coatings.

Hard coatings can be deposited by various PVD and/or chemical vapor deposition (CVD) processes including thermal spray, magnetron sputtering, plasma-enhanced CVD, ion implantation and cathodic arc deposition (CAD). Among them, CAD is
one of the most suitable technologies for its characteristics, including nearly fully ionized plasma and high energy of ions [15].

CAD systems can deposit hard coatings with high density and strong adhesion. However, the conventional planar arc systems usually deposit hard coatings with macro defects, including both inclusions and voids, due to the incorporation of the micro-metal droplets emitted from the cathodes, which also reduce the corrosion resistance of hard coatings [16]. Recently, a new cathode arc technology based on rotating cathodes was developed and included into an advanced coating system π80 developed by PLATIT [17]. The specially designed permanent and coil combined magnetic fields in the rotating cathodes and the asymmetric arrangement of the cathodes with respect to the samples to be coated enable a pre-cleaning of the cathodes by means of a Virtual Shutter® that effectively reduces the emission of droplets and significantly improves the performance of the coatings.

In this work, CrAlN and TiAlN coatings were deposited on stainless steel substrates by a Platit π80 system under a reactive nitrogen atmosphere. The corrosion behavior of the as-deposited CrAlN and TiAlN coatings in a NaCl solution was tested and compared by an electrochemical method.

2. Experimental details

CrAlN and TiAlN coatings, with a thickness of around 3 μm, were deposited by a Platit π80 lateral rotating cathodes arc system. One Cr (or Ti) and one Al elemental cathodes were used in this work, which were laterally rotating during coating deposition. The coating deposition was carried out in a flowing pure nitrogen atmosphere under a working pressure controlled at 1.5 Pa. In order to control the atomic ratio of Al/Cr (or Al/Ti) in the as-deposited coatings, the DC current applied on the two cathodes, $I_{Al}$ and $I_{Cr}$ (or $I_{Ti}$), was changed in opposite directions between 0 and 125 A with different current ratio of $I_{Al}/I_{Cr}$ (or $I_{Al}/I_{Ti}$). Mirror-finished stainless steel disks with a diameter of 50 mm were used as substrates for coating deposition. At first, the substrates were ultrasonically cleaned in a series of alkaline solutions, washed in deionized water, and dried by blowing nitrogen gas and further dried in an oven at 100 °C. Then the pre-cleaned substrates were mounted on a carrousel substrate holder which rotated continuously around the vertical central axis at a speed of 12 rpm. During deposition, a negative DC bias of −70 V was applied to the substrates. And the substrate temperature during deposition was controlled at around 480 °C.

After deposition, the coatings’ composition was measured by energy dispersive analysis of X-rays (EDX), which is attached to a scanning electron microscope, at 8 keV and the INCA quantitative analysis software. Alumina, titanium and chromium were used as the reference materials for quantitative analyses. The surface roughness of the coatings was measured by a profilometer with a scan length of 20 mm. The coating crystalline structure was analyzed by X-ray diffraction (XRD) which was performed on a Philips x-ray diffractometer in a 0–20 scan mode using CuKα radiation (40 kV, 30 mA). The scanning step size and the counting time at each step were set as 0.05° and 10 s, respectively.

The corrosion behavior of the coating system was tested by an electrochemical method, i.e. potentiodynamic polarization measurement. The test cell used was a critical pitting test cell from Gamry Instruments, USA, with an active area of 0.90 cm². A three electrode system was used, consisting of a saturated calomel electrode (SCE) as a reference, a pure graphite counter electrode and the coated sample under test as the working electrode. The electrolyte employed was 3 wt.% sodium chloride solution, prepared with analytical grade reagents and deionized water. Before the electrochemical measurements, samples were allowed to stabilize at their open circuit potential for 30 min. Potentiodynamic polarization measurements were carried out starting from −0.20 V cathodically with respect to the open circuit potential. Thereafter, the sample was polarized anodically with a scan rate of 0.5 mV/s.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-deposited coatings. Both the CrAlN and TiAlN coatings were crystallized into a rocksalt-type cubic structure. Besides the XRD peaks arisen from the steel substrate (marked as SS in the figure), three diffraction peaks, (111), (200), and (311), can be clearly identified from the XRD patterns of the CrAlN, as shown in Fig. 1(a). Generally, the intensity of all these three diffraction peaks decreased gradually with increasing Al/Cr atomic ratio, implying that the coating crystallinity decreased or the crystallinities in the coatings became finer with the incorporation of Al. This fact could be attributed to the lattice distortion caused by aluminum incorporation. Unlike the CrAlN coatings, TiAlN coatings, as shown in Fig. 1(b), show an evident (111) preferential orientation, with only the (111) diffraction peak (including its second order peak (222)) being clearly observed. Moreover, the intensity of the (111) peak decreased rapidly with the incorporation of Al into the coatings. This indicates that the Al incorporation results in a finer structure or a decrease of the crystallinity or even becoming partially amorphous of the coating.

In our previous work [12], CrAlN coatings with lower Al content (atomic ratio Al/Cr<0.6) were deposited by DC magnetron
sputtering. Those coatings were not well-crystallized due to the lower substrate temperature (no deliberating heating was applied) during the coating deposition process. The pure CrN coating even showed an X-ray amorphous structure. With the increase of Al content in the coatings (by increasing the sputtering current applied onto the Al targets) up to Al/Cr \( \approx 0.3 \), the crystallinity improved gradually due to the increased ion bombardment. With Al further incorporation (Al/Cr > 0.3), the coating crystallinity decreased due to the lattice distortion. In the present work, all the coatings are well-crystallized, as seen from Fig. 1. On one hand, the crystalline structure was well formed due to the high substrate temperature being controlled at 480 °C during coating deposition. On the other hand, the extreme high ionization percentage of the depositing species in the arc deposition process plays an important role for promoting the crystalline structure formation.

Fig. 2 shows the (111) diffraction peak position of the CrAlN and TiAlN coatings as a function of Al/Cr or Al/Ti atomic ratio. It is noted that, for both the CrAlN and TiAlN coatings, the (111) diffraction peak shifted to the higher angle side, indicating a decrease of lattice parameters, gradually with increasing the Al/Cr or Al/Ti atomic ratio. This phenomenon indicates the formation of the alloy nitride CrAlN or TiAlN and the lattice shrinking fact could be ascribed to the substitution of chromium or titanium atoms by the smaller aluminum atoms.

Fig. 3 shows typical potential polarization curves of the CrAlN-and TiAlN-coated samples. Both of them show an evident passive stage. In the passive potential range, the corrosion current remains at a very low level of around 2 \( \times 10^{-6} \) A/cm². However, when the potential was increased to a certain value, there was an abrupt increase in corrosion current, showing a clear breakdown characteristic of the coating/substrate system. Visible inspection of the sample before and after the potentiodynamic corrosion test in an optical microscope and SEM revealed that pitting corrosion has occurred. Fig. 4 is an SEM photograph showing a typical pitting corrosion on the coating surface after the potential polarization test. The cause of this type of corrosion was a macroscopic defect (pore) within the coating. The critical potential above which the corrosion current increases abruptly can be defined as “pitting potential”, and the increase of pitting potential \( (E_{\text{pit}}) \) to a more positive value can be taken as an indication that the coating/substrate system is getting more corrosion resistant. The existence of the passive region is due to the spontaneous formation of a thin oxide passive layer on the external surface \([18–20]\) when the coating is contacting the NaCl solution, which seals pores in the coating, inhibiting electrolyte diffusion to the steel substrate surface. However, when the polarization becomes too positive, pitting occurs due to the dissolution of the originally formed oxide layer.

Fig. 5 shows the pitting potential of the TiAlN and CrAlN coatings, as a function of Al/Cr or Al/Ti atomic ratio. It was found that for both the coating series, the best corrosion resistance was obtained in the coating with an Al/Cr or Al/Ti atomic ratio at around 1.0. When studying the corrosion behavior of the multilayered WC–Ti\( _{1-x} \)Al\( _x \)N and WC–(Cr\( _{1-x} \),Al\( _x \))N coatings, S. H. Ahn et al. \([21,22]\) also found that the best corrosion resistance...
of the two coating systems was obtained at around $x = 0.5$, which is similar to the experimental results in our present work.

It is well known that the corrosion properties of the hard coatings largely rely on their microstructure. Monolayer PVD hard coatings were usually grown in columnar structure, particularly for the TiN coatings. The columnar structure leads to straight grain boundaries and open (through coating) porosity [23] which provides efficient diffusion channels for the corrosive electrolyte penetrate down to the substrate. With the incorporation of Al into the TiN or CrN, the coating structure becomes finer and finer, as observed from the XRD patterns shown in Fig. 1. This results in the discontinuous crystallite boundaries in the columnar structure, which decrease the opportunity for the through coating defects or open pore to form. The diffusion of reactants through the finer-grained coating must take a zigzag route, so that the diffusion process is slow and difficult. And as a consequence, the corrosion resistance of the finer-structured coating/substrate system is improved. Similarly, M.A.M. Ibrahim et al. [24] also reported that by ‘alloying’ of the binary TiN coating with Al to form the ternary TiAIN, the corrosion resistance of the as-derived coating/substrate systems can be effectively improved in both borate and NaCl aqueous solutions. However, with the further increase of the Al content in the CrAlN or TiAlN coatings, the coating roughness increased, as measured by a surface profilometer and shown in Fig. 6, because of the increased incorporation of aluminum microdroplets emitted from the Al cathode due to its lower melting point. The increased coating roughness would result in an increase of defects, could be both inclusions and pin-holes, in the coating which would consequently reduce the corrosion resistance of the coating system.

From Fig. 5, it is also noted the corrosion resistance of the CrAIN coatings is evidently better than that of the TiAIN coatings. There are several possible causes which could be responsible for the better corrosion resistance of CrN-based coatings over TiN-based coatings. According to Liu et al. [23], their SEM observation results clearly showed that TiN PVD coating exhibited an evident columnar structure. In comparison with TiN, CrN coating had denser and finer and non-columnar microstructure, which restricts the diffusion of reactive species down to the coating/steel substrate interface. Our XRD analysis results (see Fig. 1) demonstrated that TiN-based coatings, esp. TiN, showed a strong (111) preferential orientation, while CrN-based coatings showed a random orientation. These results could also be an indirect indication that TiN-based and CrN-based coatings are of columnar and non-columnar structure, respectively. This structure difference could be one direct reason being responsible for the better corrosion resistance of CrN-based coatings.

Both TiN and CrN coatings could spontaneously form a very thin passive oxide layer [20] on the coatings’ top surface and at the pores when the coating samples are contacting with the NaCl solution. This passive oxide layer eliminates localized corrosion and protects the stainless steel substrate from degradation at the pinholes. However, Cr is known to form dense oxide layers with excellent corrosion and oxidation resistance [25,26], while Ti usually forms porous-structure oxide layers [6] which is less-protective to the steel substrates. In Ref. [20], the better corrosion resistance afforded by CrN than TiN is also explained by the formation of a thin oxide passive film with favorable semiconductive properties. Through
a detailed analysis of the electrochemical impedance spectroscopy, it was established that the spontaneously formed passive oxide layers on CrN and TiN surface present p- and n-type semiconductive characteristics, respectively. From a corrosion point of view, nitrides based coatings are known to be often cathodic when deposited onto steel substrates. The beneficial corrosion-resistant effect of CrN coating is due to the formation of the favorable p-type semiconductive oxide layer, which significantly slows down the reduction kinetic, thus also the corrosion rate.

4. Conclusion

Two series of CrAlN and TiAlN coatings were deposited on stainless steel substrate by a vacuum arc reactive deposition process from two lateral rotating elemental aluminum and chromium or titanium cathodes in a flowing pure nitrogen atmosphere. All of the as-deposited coatings were crystallized into a cubic structure. The TiAlN coatings exhibited a strong (111) preferential orientation, while the CrAlN coatings showed a random orientation. Both the CrAlN-coated and TiAlN-coated samples exhibited the best corrosion resistance in a 3 wt.% NaCl solution at a composition with Cr/Al or Ti/Al atomic ratio of around 1:1, which could be ascribed to the two competitive factors – the structural stuffing and roughness increase as Al content in the coatings is increased. With a similar composition the CrAlN coatings showed an evidently better corrosion resistance than the TiAlN coatings.

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References