Structural evolution and electrochemical behaviors of multilayer

Al-Cr-Si-N coatings

Mohan Chen, Wanglin Chen, Fei Cai, Shihong Zhang^{*}, Qimin Wang

School of Materials Science and Engineering, Anhui University of Technology, Maanshan City,
Anhui Province 243002, PR China.

*Corresponding author: Tel & Fax number: +86-555-3553789; Email address:
tougaoyouxiang206@163.com

Abstract: The corrosion behaviors in 3.5% NaCl and 10% H₂SO₄ solutions of the nano-composite Al-Cr-Si-N coatings, deposited on stainless steel 316L substrates using multi-arc ion plating process, annealed at 700°C, 800°C and 900°C, each for 2 hours, was studied. The phase structures, surface morphologies, adhesion strength, and corrosion properties of the Al-Cr-Si-N coatings before and after vacuum annealing were investigated. Results indicated that, with increasing annealing temperature, the phase structures of the nano-composite Al-Cr-Si-N coatings varied from solid solution (Cr,Al)N phase to CrN, Cr₂N and AlN phases with a hexagonal close packed structure (hcp-AlN), and then to CrN, Cr₂N, hcp-AlN and Cr phases, and finally to CrN, Cr₂N, hcp-AlN, Cr and σ -FeCr phases. The defects on the coating surface were decreased simultaneously. The samples annealed at 800°C had the highest adhesion strength. The potentiodynamic polarisation measurements showed that the corrosion resistance of coatings were improved after annealing. The coatings annealed at 800°C had the best corrosion resistance in 3.5% NaCl solution, and the coatings annealed at 700°C had the best corrosion resistance in 10% H₂SO₄ solution.

Keywords: Multi-arc ion plating; Al-Cr-Si-N coatings; Vacuum annealing; Corrosion resistance

1 Introduction

Nano-composite ceramic coatings, which were prepared by physical vapor deposition (PVD) technology, played an important role in the surface modification of engineering components in various industrial environments owing to their properties such as high hardness[1-3], good tribological properties[4-5], oxidation resistance[6-8] and corrosion resistance[9-11]. However, these coatings exhibited growth-related defects such as micro-cracks, particles and droplets[12-14]. These defects created a direct path between substrate and corrosive media, which would affect the corrosion resistance behavior of these coatings.

To improve the corrosion properties of these PVD coatings, several methods had been used. For example, C. Liu et al.[15] found that the improvement of corrosion resistance was not only attributed to the increase in the coating thickness, but also to the internal microstructure (dense non-columnar structure) and phase composition(mixture of α -Cr, β -Cr₂N, γ -CrN phases). M.S. Ahmed et al.[16] reported that the oxide layer formed from coatings surface and reduction of residual stress could increase the corrosion resistance of TiSiN coatings after 900 °C annealing. In addition, the nano-composite and multilayer structures, incorporation of the interlayer (such as PVD Al, Si etc.)[9,16-19] and alloying of the coatings (i.e. ternary coatings) were helpful to achieve high corrosion resistance by controlling the size and the density of the micro-pores.

The studies on PVD coatings was last for years, but studies on AlCrSiN coatings were limited, and mostly focus on the hardness, tribological properties and oxidation

resistance[20-23]. Polcar et al.[24] found that AlCrSiN coatings had better oxidation resistance than CrAlN coatings, these coatings also had good tribological properties when temperature blow 500 °C. Zhang et al.[8,20] deposited a superhard CrAlSiN superlattice coatings by multi-arc ion plating(M-AIP), indicated that the coatings exhibited good thermal stability and oxidation resistance when temperature up to 900 °C. The wear test showed that the superhard CrAlSiN coatings has a very low friction coefficient against the counterpart material of WC/Co. Lee et al.[22] also reported that AlCrSiN coatings exhibited good oxidation resistance between 800 °C and 1000 °C. But, more remarkable, the research on corrosion resistance of AlCrSiN was more rarer. Lin et al.[25] using electrochemical impedance spectroscopy(EIS), studied corrosion performance of CrAlSiN with different Si content coated steels in 3.5% NaCl solution, indicating a significant increase of charge-transferred resistance with increasing Si content. It's worth mentioning that the research on corrosion resistance of AlCrSiN coatings after high temperature annealing is still blank.

In this work, X-ray diffraction(XRD), field emission scanning electron microscopy(FESEM), energy dispersive spectroscopy(EDS) and high resolution transmission electron microscopy(HRTEM) were used to characterize the microstructure evolution. The adhesion strength of coatings were investigated by scratch test combined with Rockwell indentation, and the corrosion behaviors of coatings before and after vacuum annealing were investigated by potentiodynamic polarisation measurements in 3.5% NaCl and 10% H₂SO₄ solutions.

2 Experimental details

2.1 Preparation of samples

The Al-Cr-Si-N coatings investigated in this research were deposited on stainless steel 316L (SS 316L) substrates using M-AIP equipment equipped with 12 sets of standard cathodic arc ion evaporators (three cathode Cr targets(99.9% purity), three AlCrSi targets (46 at.% Al, 46 at.% Cr, 8 at.% Si, 99.9% purity) and three AlCr targets(70 at.% Al,30 at.% Cr, 99.9% purity)). The AlCrSi and AlCr targets were symmetrically installed on the opposite side of the barrel-shaped vacuum chamber wall. The SS 316L substrates (3 mm × Φ 14 mm) were polished to an average surface roughness ($R_a \leq 0.05 \mu\text{m}$) to obtain a mirror-like surface and then ultrasonically cleaned in acetone and alcohol for 15 min, respectively. The substrates were placed into the deposition chamber, with a substrate–target distance of 200 mm, being held by a star-like rotation bracket and rotating at a speed of 4 rpm.

Before deposition, the chamber was decreased to a base pressure below 1×10^{-3} Pa, the substrates were heated and kept at a temperature of 450 °C, and then the samples were first cleaned by Ar ions bombardment (Ar, 99.99% purity, flow rate of 80 sccm) at bias voltage of –1000 V for 30 min. The next step was to deposit CrN and Al-Cr-N interlayers to improve adhesion strength and reduce stress in the interface. At last, the Al-Cr-Si-N coatings were deposited using the AlCrSi targets and AlCr targets, simultaneously. All the deposition process were carried out in N₂, and the detailed depositional parameters of each layer had been summarized in Table 1. After deposition, the samples were annealed at temperatures of 700 °C, 800 °C and 900 °C for 2 hours conducted in a vacuum annealing furnace with a heating rate of 10 °C/min,

separately. The base vacuum degree of the furnace was 3.0×10^{-2} Pa. After annealing, the samples were cooled to room temperature in vacuum before being removed from the furnace to prevent oxidation.

2.2 Properties tests

The corrosion behaviours of the Al-Cr-Si-N coatings before and after annealing was investigated by potentiodynamic polarisation measurements with a conventional three-electrode cell, in which, sample used as the working electrode was placed in Teflon sample holder and the exposed surface area to the corrosive medium was approximately 1 cm^2 . The platinum strip of 1 cm^2 area served as the counter electrode and a saturated calomel electrode (SCE) as a reference electrode was used. The corrosion measurements were carried out in 3.5% NaCl solution and 10% H_2SO_4 solution respectively at room temperature, non-stirred and free air conditions. Potentiodynamic polarisation measurements were performed using the CHI604D system. To establish a steady state potential, the sample was immersed in the solution for 1 hour. The polarisation curves were obtained with a scan rate of 1 mV/s . The corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were deduced from the Tafel plots.

2.3 Characterization

The adhesion strength of samples before and after annealing was measured by a scratch tester (HT-3001 scratch tester equipped with an acoustic emission detector)

combined with Rockwell indentation. X-ray diffraction (XRD, BrukerD8 Advance) with a wavelength of 0.15406 nm Cu-K α radiation was used for analyzing the crystallographic phase transformations in the coatings before and after annealing. The scans were recorded in a range from 30° to 90° with a step width of 0.02° at 3°/min. The microstructure of the coatings were investigated by high resolution transmission electron microscopy (HRTEM, FEI-F20), and samples for TEM were prepared using a dual-beam focus ion beam (FIB) microscope. Surface morphologies and chemical compositions of the coatings were observed using a field emission scanning electron microscopy (FESEM, FEI-NANOSEM 430) with energy dispersive spectroscopy (EDS) for elemental analysis.

3 Results and discussion

3.1 Phase evolution

The XRD diffraction patterns of as-deposited Al-Cr-Si-N coatings and the coatings vacuum annealed at 700 °C, 800 °C and 900 °C are shown in Fig. 1. The annealing temperature strongly affected the structures of Al-Cr-Si-N coatings. The diffraction peaks of the as-deposited Al-Cr-Si-N coatings located at 37.62° and 63.71° were CrN phases, which were shifted toward to higher angles compared with standard PDF cards. This reflected the formation of (Cr, Al)N solid solution phases, where Cr atoms was replaced by Al atoms in the CrN lattice. After 700 °C vacuum annealing, the coatings were mainly composed of AlN with hexagonal closepacked structure (hcp-AlN) and Cr₂N phases, which indicated that the (Cr, Al)N solid

solution were decomposed at 700 °C. When the annealing temperature reached 800 °C, the (Cr, Al)N solid solution phases were further decomposed and some pure α -Cr crystalline phases diffraction peaks were detected, which implied Cr_2N decomposes to α -Cr phases and N_2 . H. Willmann et.al[26] and Pang et.al[27] also found that the Cr_2N decomposition resulted in α -Cr at high annealing temperatures. Then the annealing temperature further increased to 900 °C, results in much stronger intensities of the hcp-AlN, Cr_2N and α -Cr phases contrasted with the results at annealing temperature of 700 °C and 800 °C. Additionally, new diffraction peaks of σ -FeCr phases were observed, which indicated some iron atoms from substrates diffused to the coatings, combined with chromium atoms then formed FeCr solid solutions. The diffraction peaks of σ -FeCr phases, of SS 316L annealed at 900 °C were not found in Fig. 1, it can be concluded that the σ -FeCr phases formed from coatings rather than the substrates during vacuum annealing.

Fig. 2 shows the transmission electron microscopy(TEM) micrographs of as-deposited Al-Cr-Si-N coatings. Fig. 2a is the cross-sectional morphologies of the coatings, in which, the thickness of coatings was about 3.3 μm . The as-deposited Al-Cr-Si-N coatings exhibited a fine-grained dense morphology, including the adhesive sublayer, AlCrN interlayer and outer layer of AlCrSiN, respectively. Fig. 2b presents nanocrystalline diffraction rings of AlCrN interlayer. The selected area electron diffraction (SAED) pattern shows CrN phase and no diffraction spots of containing aluminum phase, such as AlN phase, can be found. It can be concluded that Cr atoms was replaced by some Al atoms in the CrN lattice, and formed (Cr, Al)N

solid solution in AlCrN interlayer. Fig. 2c shows the HRTEM morphology of outer layer of AlCrSiN, which exhibited superlattice structure with a modulation period of 8 nm. The high magnification morphology of AlCrSiN layer is also shown in Fig. 2c, which demonstrated that the superlattice structure consisted of alternating nanocrystalline layer and amorphous(Si_3N_4) layer[21].

Fig. 3 shows the SAED patterns of Al-Cr-Si-N coatings vacuum annealed at 800°C. The SAED pattern of AlCrN interlayer is shown in Fig. 3a, which was demarcated as CrN and Cr_2N phases, respectively, and have an approximate crystal orientation relationship: $(002)_{\text{CrN}} // (0002)_{\text{Cr}_2\text{N}}, [011]_{\text{CrN}} // [0110]_{\text{Cr}_2\text{N}}$ and $(022)_{\text{CrN}} // (\bar{2}110)_{\text{Cr}_2\text{N}}$. It indicated that the CrN phases were decomposed during vacuum annealing. The SAED pattern of AlCrSiN layer(Fig.3b) identifies that the AlCrSiN layer was composed of nanocrystalline fcc-CrN phase and hcp-AlN phase. J.L. Endrino et.al[28] studied the spectral evidence of spinodal decomposition, phase transformation and molecular nitrogen formation in supersaturated TiAlN coatings upon annealing, and found that the c-AlN phase transformed into the thermodynamically more stable hcp-AlN when the vacuum annealing temperature $\geq 900^\circ\text{C}$. However, the formation temperature of hcp-AlN phase was about 800 °C in this study, this is mainly because of the influence of the Si element or superlattice structure.

Fig. 4 shows the HRTEM images of Al-Cr-Si-N coatings after vacuum annealing at 900°C. Fig. 4a shows the cross-sectional morphologies of the coating after 900°C vacuum annealing. The grain boundary of AlCrSiN layer became much fuzzier compared with the as-deposited coatings. It indicated that the high enough

temperature of vacuum annealing caused phase transformation and elemental diffusion, which damaged the superlattice microstructure of the coatings. The SAED pattern of AlCrSiN layer (Fig. 4b) confirmed the existence of pure α -Cr phase, and this result was also supported by the XRD of Al-Cr-Si-N coatings after 900°C annealing, which indicated the Cr₂N phases further decomposed to α -Cr phase during 900°C annealing.

3.2 Surface morphologies

The surface morphologies of Al-Cr-Si-N coatings before and after vacuum annealing was observed by FESEM as shown in Fig. 5. Some defects were presented on the surfaces, such as the solid or liquid particles, droplets and pinholes. These defects were typical characteristics of AIP technology. The EDS patterns indicate the particles were mainly comprised of Al, Cr and Si, indicating that these particles were pure Al, Cr or Al-Cr alloy. The particles were derived from the surface of the cathode material, which were local heated by the cathode spots higher power and became the molten pools. The liquid metal were sputtering deposited directly on the surface of the samples and became droplets and pinholes. Fig. 5b shows the liquid particles deposited on the coatings, which caused by the droplets shrinking. These defects easily become the channels of corrosive media, and accelerated the destruction of coatings. As shown in Fig. 5a to d, when the vacuum annealing temperatures increased from 700 to 900 °C, the number and size of surface defects evidently decreased, which contributed to the pure Al and some Al-Cr alloy melted made the

pinholes to be filled.

3.3 Adhesion strength

The Rockwell indentation and scratch test were generally accepted as two simple and effective methods in evaluating adhesion strength between coatings and substrate. The scratch test process could be divided into three stages (Lc1, Lc2, Lc3), and the load corresponding to the complete peeling of coating was termed the higher critical load Lc2, which was considered as adhesion strength of coatings[29]. Fig. 6 presents the Rockwell indentation and scratch test results of Al-Cr-Si-N coatings vacuum annealed at 700 °C, 800 °C and 900 °C, respectively. A number of cracks were discovered around the edge of the Rockwell indentation in Fig. 6a, b and d, but no chippings can be found, which indicated all the coatings exhibited good adhesion strength between the coatings and substrates. However, Fig. 6b and d had less cracks compared with Fig. 6a, and almost no cracks were found in Fig. 6c, which meant the Al-Cr-Si-N coatings annealed at 800 °C had the highest adhesion strength. The scratch test results of Al-Cr-Si-N coatings corresponding to the critical adhesive loads Lc2 in Table 2, which indicated that the adhesion strength between coatings and substrate was greatly improved with the annealing temperature increasing except the results in 900 °C, and the scratch test results were extremely consistent with the results of Rockwell indentation.

As a result, the adhesion strength of coatings was greatly improved with the increasing annealing temperature owing to the reduction of residual stress and

structural defects[16]. However, when the annealing temperature reached 900 °C, the critical load L_{c2} decreased, It mainly caused by the formation of negative σ -FeCr phases, and the σ -FeCr phases were hard and fragile, which could decrease the ductility of coatings[30].

3.4 Electrochemical performance

Fig. 7 shows the potentiodynamic polarisation curves of the Al-Cr-Si-N coatings before and after vacuum annealing in 3.5% NaCl solution. The corrosion potential (E_{corr} , V), the corrosion current(i_{corr} , A.cm⁻²) and the polarisation resistance(R_p , Ω .cm²) were obtained from these curves are displayed in Table 3. The E_{corr} of as-deposited coatings was about -0.238V, and the i_{corr} was about 2.787×10^{-8} A.cm⁻². After 700 °C vacuum annealing, the E_{corr} of coatings increased to -0.178V, and the i_{corr} decreased to 5.438×10^{-9} A.cm⁻². Similarly, the E_{corr} of coatings increased to 0.045V after 800 °C vacuum annealing, and the i_{corr} decreased to 8.805×10^{-10} A.cm⁻². However, the E_{corr} of coatings annealed at 900 °C was lower than 800 °C , but still shifted toward more positive than others, which indicated the corrosion resistance of the coatings was greatly improved after vacuum annealing, and the 800°C annealed coatings had the best corrosion resistant properties.

$P(\%)$ (Table 3) was obtained by the following equation[31], which represented the protective efficiency, and calculated from the potentiodynamic polarisation data.

$$P(\%) = (1 - i_{corr}/i_{corr}^0) \times 100\% \quad (1)$$

Where i_{corr} and i_{corr}^0 denoted the corrosion current densities of the bare and

covered electrodes, respectively. As listed in Table 3, with the increasing annealing temperature, the protective efficiency was 84.53%, 97.50% and 97.07%, respectively. The 800 °C annealed sample had the highest $P(\%)$ in 3.5% NaCl solution.

Similarly, Fig. 8 shows the potentiodynamic polarisation curves of the Al-Cr-Si-N coatings before and after vacuum annealing in 10% H₂SO₄ solution, and the corresponding corrosion parameters are listed in Table 4. It was obvious that the E_{corr} of coatings annealed at 700 °C was more positive than coatings in other conditions. The corresponding i_{corr} decreased about four orders of magnitude compared with as-deposited coatings, and the $P(\%)$ was the highest, which indicated the coatings had the best corrosion resistance in acid environment after 700 °C annealing.

In short, the corrosion resistance of the nano-composite Al-Cr-Si-N coatings were improved obviously after vacuum annealing at various temperatures. The number and size of surface defects evidently decreased when vacuum annealing temperatures increased from 700°C to 900 °C, which could be considered as one of the reasons to improved the corrosion resistance of the coatings. The difference in the corrosion resistance of the coatings were also related to the microstructure variation of coatings. The Si element was mainly existed in the form of amorphous Si₃N₄, which were proved in the analysis of HRTEM. The amorphous Si₃N₄ had very good corrosion resistance owing to its dielectric nature and dense microstructure without preferential corrosion paths like grain boundaries and other structural defects. Moreover, the addition of Si₃N₄ could decrease the crystallite size and enhance the

dense of coatings microstructure[32]. On the other hand, the coatings showed nano-multilayer superlattice structure, which blocked the path of corrosion medium. Therefore, the as-deposited coatings exhibited good corrosion resistance. When the vacuum annealing temperatures reached 700 °C, the coatings were given priority to hcp-AlN and Cr₂N ceramic phases, which were believed to be responsible for the enhanced corrosion behavior compared with the as-deposited coatings. After 800°C vacuum annealing, the coatings mainly existed as hcp-AlN, CrN, Cr₂N and a small amount of α -Cr phases. The α -Cr and CrN phases also had good corrosion resistance in NaCl aqueous solution. Whereas, Masami Taguchi et al.[33] reported that the pure Cr, mixtures of α -Cr + Cr₂N were rapidly attacked in 10wt% H₂SO₄ solution, and in a mixture of Cr₂N + CrN, Cr₂N was selectively corroded. Therefore, the corrosion resistance of the coatings annealed at 800°C were further enhanced in 3.5% NaCl solution, but reduced in 10% H₂SO₄ solution. However, the σ -FeCr phases were detected in the coatings annealed at 900°C, which easily produced a significant corrosion attack[34]. Meanwhile, the superlattice microstructure of the AlCrSiN coatings was damaged during 900°C annealing, which was greatly affected the corrosion resistance of the coatings. Hence, the corrosion potential of coatings were more negative, and the corrosion resistance of coatings were farther decreased.

4 Conclusions

In this study, the microstructures, surface morphologies, adhesion strength and corrosion resistance of the nano-composite Al-Cr-Si-N coatings annealed at different

temperatures were investigated. The as-deposited coatings mainly composed of the solid solution (Al,Cr)N. With increasing annealing temperature, the solid solution (Al,Cr)N decomposed into CrN, Cr₂N and hcp-AlN phases, and then the CrN phase further decomposed into Cr₂N and Cr With N₂. Then the Cr atoms formed σ -FeCr with Fe atoms which spread into substrates. Superlattice structure appeared in the nano-composite Al-Cr-Si-N coatings, and the Si element mainly existed in the form of amorphous Si₃N₄. But the superlattice structure was damaged after 900 °C annealing. With the increasing annealing temperature, the number and size of some defects gradually decreased in the nano-composite Al-Cr-Si-N coatings. The Rockwell indentation and scratch tests indicated that the coatings annealed at 800 °C had the best adhesion strength between coatings and substrates among all series. Because of structural optimisation and improvement on surface defects and interface adhesion, the corrosion resistance of annealed coatings were better than SS316L, and coating annealed at 800°C had the best corrosion resistance in 3.5% NaCl solution. When the corrosion medium was 10% H₂SO₄ solution, the coatings annealed at 700°C had the best corrosion resistance.

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Figure captions

Figure 1 XRD diffraction patterns of as-deposited AlCrSiN coatings and vacuum annealed coatings at temperatures of 700 °C, 800 °C and 900 °C.

Figure 2 The HRTEM images of as-deposited AlCrSiN coatings: (a) Cross-sectional morphologies image, (b) The SAED pattern of AlCrN interlayer, (c) High resolution morphologies.

Figure 3 The SAED patterns of AlCrSiN coatings vacuum annealed at 800°C: (a) The SAED pattern of AlCrN interlayer; (b) The SAED pattern of AlCrSiN layer.

Figure 4 The HRTEM images of 900°C annealed AlCrSiN coatings: (a) High resolution morphologies; (b) The SAED pattern of AlCrSiN layer.

Figure 5 Surface FESEM micrographs of as-deposited AlCrSiN films (a), and coatings after vacuum annealed at temperatures of 700 °C (b), 800 °C (c) and 900 °C (d).

Figure 6 The Rockwell indentation and scratch test results of AlCrSiN coatings vacuum annealed at temperatures of 700 °C, 800 °C and 900 °C.

Figure 7 Potentiodynamic polarisation curves of the AlCrSiN coatings before and after vacuum annealing in 3.5wt% NaCl solution.

Figure 8 Potentiodynamic polarisation curves of the AlCrSiN coatings before and after vacuum annealing in 10wt% H₂SO₄ solution.

Table 1

Deposition parameters on each layer of the AlCrSiN coatings.

Various deposition parameters	CrN layer	AlCrN layer	AlCrSiN layer
Nitrogen flow rates (sccm)	800	900	900
Vacuum pressure(pa)	0.8	1.5	2
Temperature(°C)	450	450	450
Arc current of Cr cathode (A)	60	60	-
Arc current of AlCr cathode (A)	-	65	75
Arc current of AlCrSi cathode (A)	-	-	75
Bias voltage (V)	120	80	80
Time(s)	960	7200	9000

Table 2

The critical adhesive loads Lc2 of AlCrSiN coatings annealed at various temperatures.

Temperatures (°C)	As-deposited	700	800	900
Lc2 (N)	28.7	40.5	53.2	40.8

Table 3

Potentiodynamic polarisation data of the ss316L and AlCrSiN coatings before and after vacuum annealing in 3.5wt% NaCl solution

Specimen	E_{corr} (V)	i_{corr} (A.cm⁻²)	R_p (Ω.cm²)	P(%)
SS316L	-0.356	3.52×10^{-8}	1.19×10^6	—
As-deposited	-0.238	2.79×10^{-8}	7.68×10^5	20.73
700°C	-0.178	5.44×10^{-9}	5.30×10^6	84.53
800°C	0.045	8.81×10^{-10}	4.07×10^7	97.50
900°C	-0.151	1.02×10^{-9}	3.62×10^7	97.07

Table 4

Potentiodynamic polarisation data of the ss316L and AlCrSiN coatings before and after vacuum annealing in 10wt% H₂SO₄ solution

Specimen	E_{corr} (V)	i_{corr} (A.cm⁻²)	R_p (Ω.cm²)	P(%)
SS316L	-0.085	7.174×10^{-5}	6.84×10^2	—
As-deposited	0.005	7.608×10^{-6}	3.16×10^3	89.4
700°C	0.222	6.04×10^{-9}	6.63×10^6	99.99
800°C	0.054	3.691×10^{-8}	1.09×10^5	99.95
900°C	0.016	1.944×10^{-6}	2.06×10^4	97.29

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Adhesion strength (N)

Lc2
Lc3

Figure 7

Figure 8