

EFFECT OF CHROMIUM ADDITION ON MICROSTRUCTURE AND MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF TiAlN BASED COATING

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Abstract

In this research, TiAlN and TiAlCrN coatings on SKH 51 tool steel were prepared using the cathodic arc evaporation technique. The quaternary ($\text{Cr}_x\text{Al}_{1-x}\text{Ti}_{0.15}$) N coating was studied in comparison to a TiAlN coating. Coating morphology on the surface and structure from a cross-section view were studied using an optical microscope and field emission scanning electron microscope. Micro Vickers Hardness and indentation tests were used to observe mechanical property of the coating. Phase analysis was investigated using X-ray diffraction. The chemical composition difference between the coatings plays an important role in the microstructure quality, hardness, and corrosion resistance. The TiAlN coating showed a smooth surface with a columnar structure, while droplets were observed on the TiAlCrN coating surface which significantly decreased the film adhesion. The TiAlCrN coatings indicate a high hardness value of 3,284 HV and good corrosion resistance.

Keywords: Mechanical properties, corrosion resistance, TiAlCrN, TiAlN, PVD process

Introduction

SKH 51 tool steel is widely used in several industries due to it having superior characteristics, including thermal stability, high strength, and wear resistance. The heat treatment process to increase the hardening of SKH 51 tool steel is nitriding. The optimum nitriding temperature for SKH 51 tool steel is between 500°C to 550°C, since at this temperature range SKH 51 tool steel does not lose its mechanical properties (Akhtar *et al.*, 2010). Nowadays, there are many methods to modify the surface of SKH 51 tool steel. The interesting process is Physical Vapor Deposition (PVD), a coating process, which produces coating material

from a single atom or molecule level. PVD coating is an environmentally friendly process that can significantly reduce the number of toxic substances produced by conventional types of coating that involve fluid precursors and chemical reactions. Nitride layer produced from the PVD process can significantly increase the mechanical properties of tool steel (Polcar *et al.*, 2011). Titanium aluminum nitride (TiAlN) coating is used for cutting tools due its excellent mechanical properties, thermal properties and high oxidation temperature (Mayrhofer *et al.*, 2006; Chim *et al.*, 2009). However, its oxidation resistance is reduced

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when temperatures increase to 750°C to 900°C (Horling *et al.*, 2002) because TiAlN coating consists of two-phase structures, namely the c-TiN and h-AlN phases. The h-AlN phase is associated with a high nucleation barrier due to a larger atomic volume (Xu *et al.*, 2013). Many researchers have studied combining Ti, Al, Cr, and N as quaternary compounds in order to improve the oxidation, corrosion, and mechanical properties of these films at high temperature. Previous studies indicate that coating containing TiAlCrN can outperform those with TiAlN coating. A single layer TiAlCrN coating is known to exhibit greater hardness and oxidation resistance than a TiAlN coating (Fox *et al.*, 2009).

Previous research indicate that adding a small amount of Cr (less than 17 at.%) to ternary TiAlN results in a metastable solid solution of the TiCrAlN coating (Forsen *et al.*, 2012). Cr addition increases to over 60 at.% in ternary TiAlN, the results show good oxidation and mechanical properties (Lind *et al.*, 2013). Therefore, Cr content over 60 at.% was selected for this study. In the present study, quaternary compounds of (Ti, Al, Cr) N coating were synthesised by cathode arc evaporation to improve the microstructure, structural, mechanical properties, and corrosion resistance.

Materials and Methods

Sample Preparation

Tool steel grade SKH 51 and a silicon wafer were used in this study. SKH 51 tool steel with a chemical composition (wt.%) of 0.88 C, 0.45 Si, 0.40 Mn, 4.50 Cr, 0.03 P, 2.17 V, 0.03 S, 5.20 Mo, 6.70 W, and balanced Fe were used as the substrate for the mechanical and corrosion tests. A silicon wafer was used as a substrate for coating characterisation. The SKH 51 tool steel and silicon substrates were coated in the same batches. SKH 51 tool steel was cut into disks with a diameter of 30 mm and a thickness of 5 mm. The SKH 51 tool steel disks were then polished with SiC papers down to the 2,400 grit number, followed by diamond powder with a mesh size of 3 µm. Before placing all specimens into a PVD chamber, they were cleaned in acetone using an ultrasonic cleaner and stored in a desiccator before deposition.

Coating Deposition

For PVD deposition, a commercial cathodic arc evaporation system (PVD) was used, where the PVD target could be operated in the chamber. Each target had a diameter of 70 mm. Two types of target for film deposition were used, Ti_{0.50}Al_{0.50} and Cr_{0.60}Al_{0.25}Ti_{0.15} targets. The working gas pressure

of N₂ (99.999%) atmosphere was 2.6 Pa, the substrate bias was 50 V, the target current was 50 A, and the deposition temperature was 460°C. The holder rotated at a speed of 2 revolutions per minute.

Coating Characterisation

The surface morphology of the coating was observed by optical microscope (OM) and scanning electron microscope (SEM:JSM-6490LA, Jeol), while the cross-section view was observed by a field emission scanning electron microscope, (FE-SEM (JSM-7001F)). The coating's chemical composition was examined using energy dispersive spectroscopy (EDS). Phase analysis of the coating was performed by X-ray diffraction using Cu K α radiation ($\lambda = 0.15406$ nm) operating at 40 mA and 40 kV. X-ray θ -2 θ diffractograms with a 2θ range from 35 to 65 degrees. Mechanical property coating layer was determined by a Micro Vickers Hardness tester using 10 gf of normal load and duration time 15 sec. The indentation depth was controlled and calculated by Micro Vickers Hardness for eliminate effect from substrate. Adhesion test was determined by VDI 3198 indentation test. Coating layer was measured by a Calo-tester and SEM image measurement. The corrosion resistance of all the samples was studied by potentiodynamic polarisation measurement using Autolab PGSTAT 302N galvanostat/potentiostat system. A three-electrode cell was used with Ag/AgCl as a reference electrode and platinum plate as a counter electrode, while the sample acted as a working electrode. The surface area of the tested sample exposed to a corrosive medium was fixed at 353 mm². All corrosion tests were performed in 3.5% NaCl at room temperature. Start and stop potentials were fixed at -1.5 to 2.0 V, respectively. The potential scan rate was 1 mV/s.

Results and Discussion

Coating Morphology

The surface appearance before and after addition of the coating are presented in Figure 1. The coating of each condition is different in coating colour. The TiAlN coating has a cinnabar colour, while the TiAlCrN coating has a dark grey colour. The average thicknesses were between 1.9-2.2 µm, and the deposition rates of the TiAlN and TiAlCrN coatings were 0.014 µm/min and 0.012 µm/min, respectively.

Cross-section and Top Surface

The cross-section view was observed by FE-SEM and the top surface was observed by SEM, as shown in Figure 2. The TiAlN coating presents

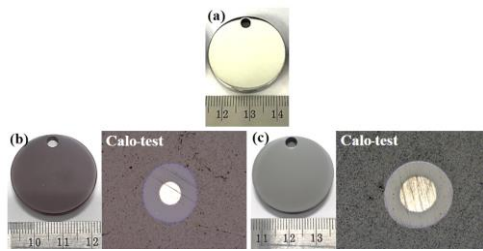


Figure 1. Surface morphology of the (a) As-coated sample, (b) TiAlN coating, and (c) TiAlCrN coating

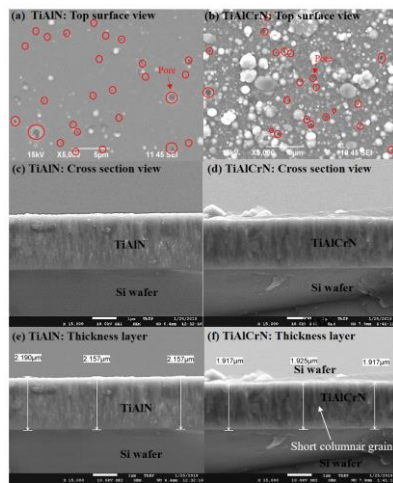


Figure 2. Cross-section and top surface of: (a) TiAlN coating: Top surface view; (b) TiAlCrN coating: Top surface view; (c) TiAlN coating: Cross section view; (d) TiAlCrN coating: Cross section view; (e) TiAlN coating: Thickness layer; and (f) TiAlCrN coating: Thickness layer

columnar grain with a large number of pores and a small number of droplets (Figure 2(a)). The TiAlCrN coating exhibited a short columnar structure (Lu *et al.*, 2014) with a small number of pores but a high number of droplets. Moreover, the droplet size of the TiAlCrN coating is significantly larger than the droplet size of TiAlN coating, as shown in Figure 2. This is due to the different Cr, Al, and Ti melting points in the targets (Fox-Rabinovich *et al.*, 2009). The melting points of Cr, Al, and Ti are at 1,860°C, 660°C, and 1,670°C, respectively. The chemical composition of the coatings were examined by using energy dispersive spectroscopy (EDS), as shown in Figure 3. The chemical composition of the target and coating layer after deposition are shown in Table 1 and confirm that the PVD process successfully fabricated the coating with a similar composition to the target.

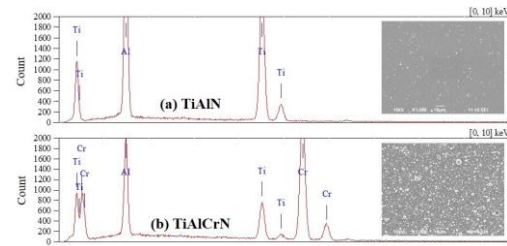


Figure 3. EDS peaks of the as-deposited coatings of (a) TiAlN coating and (b) TiAlCrN coating

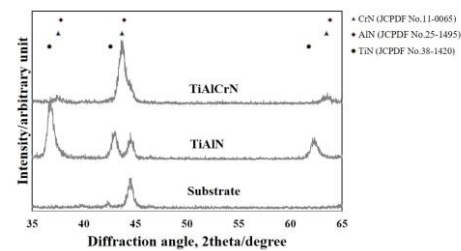


Figure 4. XRD profiles of the TiAlN and TiAlCrN coatings

Phase Analysis

Figure 4 shows the XRD profiles of the TiAlN and TiAlCrN coatings. Besides the peaks from the substrate, all the coatings show only a single set of diffraction peaks, corresponding to the FCC B-1 structure, with peaks located between the peak positions of TiN (JCPDS No.87-0633), AlN (JCPDS No. 25-1495), and CrN (JCPDS No. 76-2494) (Fernandes *et al.*, 2018). The TiAlN coating shows a (111) preferential orientation. Formation of TiAlN can be confirmed by the XRD profile. By applying data from the EDS analysis, this TiAlN is in the form of Ti_xAl_yN ($x = 0.57$, and $y = 0.43$). According to one set of B1 structure peaks in Figure 4, the formation of quaternary TiAlCrN coating can also be confirmed. The TiAlCrN coating are in the form of $Ti_xAl_yCr_zN$ ($x = 0.16$, $y = 0.22$, and $z = 0.66$) (Lin *et al.*, 2015).

Coating Layer Hardness

Table 2 presents the average hardness measurement (5points) of the coatings. The maximum hardness value was found in the TiAlCrN coating which peaked at 3284 HV. In addition, film delamination was checked by the VDI 3198 indentation test, as showed in Figure 5. The TiAlN sample shows micro-crack while film delamination was not detected. The TiAlCrN sample presents evidence of film delamination (Figure 5) caused by the low adhesion of the large droplets on the film surface which create gaps between the coating and

Table 1. Chemical composition of the coating layers measured by EDS (at.%)

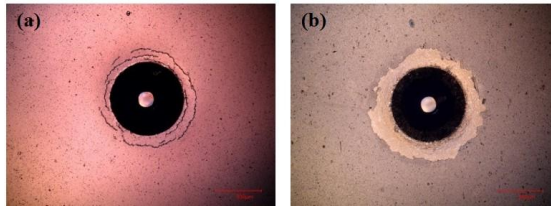
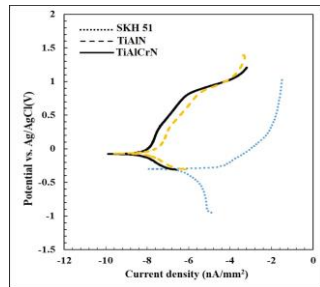
Sample Name	Target composition (at.%)			Coating composition (at.%)				Chemical formula of coating
	Ti	Al	Cr	Ti	Al	Cr	N	
(TiAlN)	0.50	0.50	-	0.57	0.43	-	0.66	$\text{Ti}_{0.57}\text{Al}_{0.43}\text{N}_{0.66}$
(TiAlCrN)	0.15	0.25	0.60	0.16	0.22	0.66	0.58	$\text{Ti}_{0.16}\text{Al}_{0.22}\text{Cr}_{0.66}\text{N}_{0.58}$

Table 2. Substrate hardness value of the TiAlN and TiAlCrN coatings

Sample	Hardness (HV)	Standard Deviation (S.D.)
SKH 51 (Substrate)	755	6.09
TiAlN	2029	33.86
TiAlCrN	3284	68.85

Table 3. The electrochemical results of the substrate, TiAlN sample, and TiAlCrN sample

Sample	i_{corr} (nA/mm ²)	E_{corr} (mV)	b_c (mV/dec)	b_a (mV/dec)	R_p (k Ω)
SKH 51(Substrate)	2219.50	-294.09	11.70	189.05	2.15
TiAlN	227.80	-74.01	505.91	347.72	392.84
TiAlCrN	180.71	-79.34	355.91	429.19	920.49

**Figure 5. VDI 3198 indentation test of (a) TiAlN coating and (b) TiAlCrN coating****Figure 6. Potentiodynamic polarisation curves of the substrate and PVD sample**

the substrate, resulting in low adhesion and coating delamination during VDI pressing.

Corrosion Resistance

The corrosion potentials (E_{corr}) and corrosion current densities (i_{corr}) were investigated by Tafel extrapolation method, which indicated that the TiAlN and TiAlCrN coatings demonstrated high corrosion potential values (Figure 6). Yet clearer findings can be found by considering Tafel calculation, through which the results of E_{corr} , i_{corr} , and R_p can be obtained (Table 3). Both R_p and E_{corr}

of the TiAlN and TiAlCrN coatings were higher than the uncoated sample conditions. Additionally, spontaneous passive film formation is evident in both samples. There are two potential explanations for the better corrosion resistance of TiAlCrN coating than the TiAlN coating. First, the TiAlCrN coating has a significantly lower number of surface pores compared to the TiAlN coating. These pores provide a direct path for corrosion media to approach the coating and substrate interface (Liu *et al.*, 2001). Second, the TiAlN coating presents a columnar grain structure consisting of a large number of grain boundaries that act as a high diffusion path for corrosion media (Ding *et al.*, 2008). In contrast, the TiAlCrN shows compact and short columnar structure that can retard the corrosion media penetration, resulting in better corrosion resistance than the TiAlN film. This compact and discontinuous structure was reported to be due to the addition of Cr addition in the coating. (Danek *et al.*, 2017).

Conclusions

This paper studied the effect of adding Cr to a TiAlN coating, finding that the coating's mechanical properties and corrosion resistance can be improved by the addition of Cr. Adding Cr to the TiAlN coating significantly increased the surface hardness up to 3284 HV. Nonetheless, poor adhesion between the coating layer and substrate was found due to the large droplets on the surface. The addition of Cr also affected the corrosion resistance of the coating layer. The polarisation resistance value (R_p) of the TiAlCrN coating is found to be three times higher than the TiAlN coating.

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