Thermal Stability and Oxidation Resistance of CrAlSiN Nano-structured Coatings Deposited by Lateral Rotating Cathode Arc

Jhun Yew Cheong 1, 2, a, X. Z. Ding 1, b, Beng Kang Tay 2, c, X. T. Zeng 1, d*

1 Surface Technology Group, Singapore Institute of Manufacturing Technology, 71 Nanyang Drive, Singapore 638075
2 School of Electrical and Electronics Engineering, Nanyang Technological University, Singapore, 50 Nanyang Avenue, Singapore 639798

a cheo0052@ntu.edu.sg, b xzding@SIMTech.a-star.edu.sg, c bktay@ntu.edu.sg, d corresponding author: xzeng@SIMTech.a-star.edu.sg

Keywords: Nano-structured coating; Oxidation resistance; CrAlSiN

Abstract. In this paper, CrAlSiN coatings are deposited by a lateral rotating cathode arc technique. The high temperature oxidation behaviors of these coatings are studied in ambient atmosphere at temperatures ranging from 800ºC-1000ºC for an hour. The ternary TiAlN coating is used as the benchmark in this study. The surface morphology and chemical composition of the coating samples before and after oxidation at different temperatures are analyzed by scanning electron microscopy (SEM) equipped by energy dispersive X-ray spectrometer (EDX), glow discharge optical spectrometry (GDOS) and X-ray diffraction (XRD). The CrAlSiN coatings show much better oxidation resistance than the TiAlN coatings. TiAlN starts to oxidize from 800ºC and forms a complete surface oxide layer after oxidation at 1000ºC for an hour. However, CrAlSiN shows a relatively good oxidation resistance below 1000ºC and only is oxidized to form a thin oxide scale with a thickness of 0.3 µm at 1000ºC for one hour. It is found that the oxidation of both coatings is triggered from the surface metallic droplets generated by the arc deposition process.

Introduction

Metallic nitride based hard coatings have been widely used in the industry for protecting the surface or prolonging the lifetime of various machining tools such as cutting tools, forming tools and dies and molds as well as wear components [1-5]. The critical factors determining the performance and lifetime of these coatings include their mechanical properties such as adhesion, hardness and toughness, oxidation resistance and thermal stability, and friction coefficient of the coating against the counterpart material. The Ti-based hard coatings deposited via PVD techniques have demonstrated high hardness and good thermal stability, particularly when Al element is introduced into the system to partially replace Ti to form an alloy solid solution structure, which results in higher hardness and an associated increase in wear resistance. More importantly, the introduction of Al element demonstrates significant improvement in coating chemical stability and oxidation resistance due to the formation of the protective Al2O3 layer at elevated temperatures. As one of the major milestones in the advances of hard coating development, TiAlN or AlTiN has been commercialized particularly for high speed machining applications due to its good oxidation resistance and high hardness over TiN. In the last decade Ti1-XAlXN coatings have become the standard choice for many applications particularly in precision engineering industry.

However, the oxidation and corrosion resistance of the titanium-based hard coatings are still limited due to the presence of Ti element which forms a porous non-protective oxide readily at high temperatures (>800ºC) due to its comparable oxygen affinity ability with Al [6, 7]. Recent studies have shown that Cr-based coatings such as CrN, CrAlN coatings exhibit improved oxidation resistance [8-13]. We have reported that the CrAlN coatings exhibit much better tribological properties than TiAlN coatings for cutting hardened steel tools [14]. We confirmed that the oxidation of Cr-based coatings is controlled by the outward diffusion of the metallic component [13] forming a protective layer of Cr2O3 [15, 16], thus improving the oxidation resistance [17]. Incorporation of Al further improves the oxidation resistance and the wear resistance [13].
Recently, much effort has been devoted to Cr-Al-Si-N nano-composite coatings, which consist of nanocrystalline grains of CrN or CrAlN embedded in a Si$_3$N$_4$ amorphous matrix [18, 19]. Such coatings demonstrated superhardness (>40Gpa), enhanced toughness, high temperature thermal stability and oxidation resistance, outstanding abrasive and erosive wear resistance. These unique properties are due to nano-crystallites embedded in an amorphous matrix, which prevents the generation of dislocations in the grains due to its nanometric size, and hinders the propagation of cracks due to grain boundary enhancement and suppression of grain boundary sliding [20, 21]. Present work studies the high temperature oxidation behaviors of cathode arc deposited Cr-Al-Si-N nanocomposite coatings in ambient atmosphere at temperatures ranging from 800ºC-1000ºC.

Experimental
CrAlSiN coatings were deposited using a Platit π$^{80}$ lateral rotating cathode arc system, which has been described previously [13]. There are two major advantages of this system over conventional planar arc systems. The first is its lateral rotating cathode which allows improved target utilization rate and prolongs the usage of the cathode and its lifetime. The second is its virtual shutter system which allows the targets and the substrates to be plasma-cleaned sequentially without cross contamination. As a result, the as-deposited coatings exhibit superior adhesion strengths and a smoother surface finish.

Deposition of the coating was performed in a pure nitrogen atmosphere with a working pressure of 1.5 Pa. Mirror-finished stainless steel (SS) disks with dimensions of 50 mm in diameter were used as substrates. The substrates were ultrasonically cleaned in a 3 stage alkaline solution, rinsed with deionized water, blown with nitrogen gas and lastly dried in an oven at 100ºC. The cleaned substrates were then mounted onto the substrate holder which was rotated along a central vertical axis at a speed of 12 rpm. Prior to deposition, the substrates were further plasma-cleaned to remove possible contaminants. During deposition, a negative bias of ~70V was applied to the substrates to introduce ion bombardment to the growing coating surface and the substrate temperature was controlled at 480ºC.

To study the oxidation resistance of the coatings, each sample was cut into four pieces of the same size and ultrasonically cleaned before annealing. The samples were placed in a quartz crucible and annealed at different temperatures (800ºC, 900ºC, 1000ºC) for 1 hour in ambient atmosphere. The microstructure of the coating was studied using a scanning electron microscope (SEM) at 20keV. The coating composition was analyzed in-situ using the energy dispersive X-ray spectroscopy (EDX). To understand the evolution of the oxidation, the EDX analyses was done with area scan and defect scan, respectively. The area scans were focused on the areas free of droplets on the surface and the defect scans were focused on the micro-droplets on the sample surface. A Horiba Jobin Yvon glow discharge optical spectrometer (GDOS) with a 4mm glow discharge source was used to measure the composition depth profile of the coating. The crystalline structure of the coating was analyzed by X-ray diffraction (XRD) performed on a Bruckers X-ray diffractometer in the θ-2θ mode using CuK$_\alpha$ radiation (40kV, 30mA). The 2θ scanning range was set from 30º-60º.

Results and Discussion
Figure 1 shows the SEM images of the as-deposited and 900ºC annealed TiAlN and CrAlSiN samples. It was observed that there were no significant differences in surface morphology of CrAlSiN coating before and after annealing. While for TiAlN coating, oxidation was observed with white particles occurring all over the surface.

Figure 2 shows the EDX analysis of the nitrogen and oxygen at.% of TiAlN and CrAlSiN coatings annealed at different temperatures. Figure 2a shows the EDX analysis results out of the area scan, e.g. focused on the areas free of droplets, and Figure 2b shows the EDX analysis results out of the defect scan, e.g. focused on the droplets on the sample surface.
It is shown in Figure 2 that in both cases the increase in oxygen content is reciprocal to the decrease of nitrogen content. For both samples, the oxygen content in the as-deposited coating is negligible, regardless area scan or defect scan. For the TiAlN coatings annealed at 800°C, oxygen content significantly increased to ~38 at.% in the area scan and ~46 at.% in the defect scan, respectively. In contrast, CrAlSiN coatings annealed at the same temperature did not show significant increase of oxygen content in either area scan (~2.8 at.%) or defect scan (~5.5 at. %). The low overall oxygen content in CrAlSiN, with the value of defect scan nearly doubled that of the area scan, suggests that the oxidation of the sample was primarily from the metal droplets, as they accounts for a small fraction of the material. While the high oxygen content in the TiAlN coating indicates that oxidation has taken place in the TiAlN coating at 800°C. At 900°C, the oxygen content in both coatings further increases but at different rates. The TiAlN is observed to have a fast increase in oxygen content, corresponding to a rapid decrease of nitrogen to nearly zero, indicating that the coating has been nearly fully oxidized. When the temperature was further increased to 1000°C, EDX analysis showed that the oxygen content of TiAlN coating starts to be saturated, while the oxygen content of CrAlSiN coating increases quickly with the difference in area scan and defect scan diminishing, indicating that oxidation of CrAlSiN coating has taken place at temperatures between 900°C to 1000°C. This is evidently higher than that of TiAlN.

Figure 3 shows the GDOS spectra of the compositional depth profiles of TiAlN (a) and CrAlSiN (b) coatings annealed at 800°C and 1000°C for one hour, respectively. The TiAlN coating was oxidized to a depth of about 0.3 micron at 800°C and almost fully oxidized at 1000°C, which led to a significant increase of the coating thickness. In contrast, the CrAlSiN coating shows no evidence of oxidation at 800°C, and a thin oxide layer of about 0.3 micron on the top surface of coating at 1000°C. This is consistent with the EDX results.

Figure 4 shows the XRD patterns of (a) TiAlN coating and (b) CrAlSiN coating after annealed at different temperatures. The peaks indexed as Fe are from the stainless steel substrate.
Figure 4 shows the XRD patterns of the coatings annealed at different temperatures, with Figure 4a representing TiAlN coating and Figure 4b representing CrAlSiN, respectively. As reported previously [19], the as-deposited TiAlN using the same system has a polycrystalline structure with a (111) preferential orientation. Compared with typical TiN coating, TiAlN coating demonstrates a significantly suppressed XRD peak intensity with a broadened peak width, indicating a significant reduction of grain size. At 800°C, weak TiO₂ and Al₂O₃ XRD diffraction peaks were observed indicating the occurrence of oxidation at or below this temperature. At 1000°C, multiple Al and Ti oxide peaks were observed. The absence of any TiAlN peaks suggests that the coating has been nearly fully oxidized at this temperature. For CrAlSiN coating (Figure 4b), the as-deposited samples have mixed crystalline orientations of CrAlN (111) and (200). No crystalline SiNx XRD peaks were observed indicating its presence inside the coating in amorphous phase. The XRD patterns of the CrAlSiN coating remain the same when the samples were annealed at 900°C or below. Chromium oxide and aluminum oxide XRD peaks were observed in the samples annealed at 1000°C, indicating the occurrence of oxidation of the coating. The relative intensity of XRD peaks (both (111) and (200)) of CrAlN coating against the substrate reference XRD peak is increased evidently. A possible explanation is that the crystalline structure of CrAlN is enhanced due to the thermal energy provided in the annealing process. The as-deposited CrAlSiN coating has a nanocomposite crystalline structure with the nano-sized CrAlN grains embedded in the amorphous SiNx matrix. The PVD process will unavoidably introduce inter-mixing between the crystalline CrAlN and amorphous SiNx with defective phase separation, and also distorted crystalline structure inside the CrAlN grains. The thermal annealing provides energy as required to assist or complete the phase separation between CrAlN and SiNx and improve the crystalline orientation, resulting in improved crystalline perfection.

It was reported that annealing TiAlN coating in oxygen atmosphere results in formation of a two layered oxidation structure due to the difference of Gibb’s free energy in forming aluminum oxide and titanium oxide [22, 23]. The outer layer mainly consists of Al₂O₃ followed by a thinner layer of titanium oxide and oxynitride. This results in the titanium being trapped beneath the Al₂O₃ oxide layer. The formation of titanium oxide is caused by the oxygen diffusion, which leads to a reduced diffusivity of titanium through the oxide layer, resulting in an improved oxidation resistance compared with TiN coating. For CrAlSiN coating, it is believed that the substantially improved oxidation resistance is attributed to its specific compositional and nano-composite structure, as explained above, which is thermodynamically stable with overall good structural integrity. It is well known that CrN has better oxidation resistance compared with TiN. The element Cr serves the similar function as that of element Al when it comes to oxidation evolution. It forms a thin dense Cr₂O₃ layer at elevated temperatures in an oxygen environment, which provides both physical and chemical barriers for oxygen to be penetrated into underneath layers.

**Conclusion**

The oxidation behavior of CrAlSiN coating at elevated temperatures was studied and compared with TiAlN coating as the benchmark. The samples were annealed at 800, 900 and 1000°C in ambient atmosphere for one hour, and analyzed by SEM, EDX, GDOS and XRD. Oxidation of TiAlN coating was observed to start at 800°C or below from the coating surface, and penetrate into the underneath layer quickly with the increase of annealing temperature. It was nearly fully oxidized at 1000°C under the experimental conditions. In contrast, oxidation of CrAlSiN coating was observed to start at about 1000°C from the coating surface. It is concluded that the CrAlSiN nanocomposite coating demonstrates substantially improved oxidation resistance as compared to TiAlN coating. With its superior oxidation resistance and thermal stability, nanocomposite CrAlSiN is believed to be a replacement coating for TiAlN for high temperature wear protection applications such as cutting tools for high speed machining and molds and dies for liquid forging of metal alloys.
Reference